Identification, Assessment and Estimation of Ozone Layer Destruction Hazardous Substances and Substitution Strategies in Petrochemical Industries

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Abstract
Ozone layer destruction gases like halogenated hydrocarbons are used in some processes like solvent extraction, fire fighting, and as refrigerants in petrochemical industries. In this study, national acts and protocols in addition of international regulations, about ozone layer destruction gases were reviewed. According to protocols' constraints, the strategy of substitution of these gases by ozone friendly gases (with considering their potential of ozone layer destruction) was followed. For this purpose, application of destructive gases in a Petrochemical Complex as case study was assessed and estimated using mass balance method. According to results of this research, it is suggested that instead of Halon 1211, CO2 gas is used as extinguisher and R-22 is good substitute for R-12. Candidate substitutions were selected depend on those potential of ozone layer destruction and they were proposed to company to perform. Finally, substitution of gases was assessed and recommended to all of petrochemical industries in Iran.
Keywords: *Ozone Depletion Substances (ODSs), Ozone Depletion Potential (ODPs), CFCs, Halogenated hydrocarbons (halons), refrigerants, R-12, R-22*

1- Introduction
The atmosphere is one of the very few examples of a true global commons in that, it is a domain that is beyond the exclusive jurisdiction of any one nation, but one that all nations may use for their own purposes. Commons need to be regulated because they have a perverse tendency to degenerate into ruin and tragedy since everyone has an incentive for exploiting them, while no one has the incentive, or responsibility, for maintaining their integrity [1]. Only recently, within a few decades, have we realized that humanity significantly influences the global environment.
Ozone is one of the naturally occurring trace gases that make up our atmosphere. The atmosphere serves three critical functions: it provides life-giving oxygen, keeps the

earth warm, and protects us from deadly ultraviolet (UV) radiation from the sun. Most of the atmosphere consists of nitrogen and oxygen, the air we breathe. These gases do not hold heat so they do not keep us warm. They also do not protect the earth from UV rays. For those purposes you have to turn to the trace gases found in the atmosphere, commonly referred to as greenhouse gases. They are: water vapor, carbon dioxide, methane, ozone, and nitrous oxide [2].

Ozone is a particularly critical trace gas because it plays two roles. In the lower atmosphere it adds to the greenhouse gases, keeping the earth warm. But it serves a more critical function in the upper atmosphere where it blocks nearly all of the sun's deadly UV rays from reaching the earth [2].

UV rays are associated with skin cancer. The "UV index" is used in summer months to let people know how long it is safe to stay in the sun. A decrease in the ozone increases skin cancer. This is important because the ozone has been in a steady rate of depletion and holes in the upper ozone layer have developed [1].

The culprit of ozone depletion was human-produced chlorofluorocarbons (CFCs) [1]. CFCs have been released into the atmosphere for years. They are emitted in part from aerosols made with CFC propellant, refrigeration units and air conditioners. As the CFCs reach the upper stratosphere UV rays cause the gas to release free chlorine atoms. It only takes a single chlorine molecule to cause tens of thousands of ozone molecules to break down into simple oxygen. Oxygen does not filter UV rays [3]. In addition to being a naturally occurring gas, ozone is also created in the burning of fossil fuels as one component of smog. Burning fossil fuels also releases carbon dioxide into the air, thickening greenhouse gases, adding to the greenhouse effect and global warming. The danger is that very small amounts of CFC gas destroy enormous amounts of ozone [3].

The move to ban CFCs was slow but all major countries producing them phased them out by the year 2000. The CFCs already released will take another estimated 50 years to break down, and CFCs will continue to be released by old products still in use [2].

In this study, national acts and protocols in addition of international regulations, about ozone layer destruction gases were reviewed. According to protocols' constraints, the strategy of substitution of these gases by ozone friendly gases (with considering their potential of ozone layer destruction) was followed. For this purpose, application of destructive gases in a Petrochemical Complex as case study was assessed and estimated using mass balance method. After that, candidate substitutions were selected depend on those potential of ozone layer destruction and they were proposed to company to perform. Finally, substitution of gases was assessed and recommended to all of petrochemical industries in Iran.

2- Literature review

International regulatory actions (UNEP, 1987) have led to the phase out of production of CFCs, halogenated compounds (halons), and several other halocarbons. This decision has prompted significant interest in the development of possible replacements for CFCs and other industrially produced compounds [2]. As part of the development of such compounds, it is necessary to consider the potential environmental effects from their use and possible emissions into the atmosphere. Their potential effects on stratospheric ozone need to be evaluated. For these compounds to be environmentally acceptable, it is necessary to ensure that their impact on the environment is small. The concept of Ozone Depletion Potentials (ODPs) has become standard mean for evaluating the effects of a compound relative to concerns about other chemicals on stratospheric ozone [1].

With few exceptions, the CFCs, halons, and replacement compounds examined previously [2] have had atmospheric lifetimes sufficiently long that they are well mixed

in the troposphere. That is not the case for these two compounds. The ODP depends directly on the amount of a compound reaching the stratosphere.
Halocarbons are greenhouse gases that can contribute to climate change as well as being largely responsible for stratospheric ozone loss over recent decades. Because of their dual impact, they are of particular concern to the environment. Amongst the most potent halocarbons in the current atmosphere are the CFCs, like CFC-11 ($CFCl_3$) and CFC-12 (CF_2Cl_2). One molecule of CFC-11 or CFC-12 in the atmosphere is respectively, 12,400 and 15,800 times more effective a greenhouse gas than one molecule of CO_2 [3]. With the exception of the naturally occurring portions of CH3Cl and CH3Br emissions, all the halocarbons in the atmosphere are man-made.
The connection between potential environmental effects and man-made CFCs was first pointed out by Molina and Rowland (1974) [1], when they suggested that chlorine from these compounds could destroy stratospheric ozone. Research findings since then have continued to support the effect of these compounds on the global distribution of ozone. In addition, it is recognized that other gases containing chlorine and bromine, which is even more reactive with ozone than chlorine, are also affecting ozone. To a lesser extent, increasing concentrations of other gases like CO_2, CH_4, and N_2O, are also involved in chemical reactions that are affecting stratospheric ozone.
The inverse relationship between changes in ozone and UV-B radiation is well established by both theoretical analyses and observations [2]. A number of studies have shown that the corresponding increase in UV at the ground resulting from ozone depletion can lead to increased incidences of skin cancers, cataracts, and other effects on humans and animals [4].
The recognition of the harmful effect of chlorine and bromine on ozone spawned international action to restrict the production and use of CFCs and halons and protect stratospheric ozone. These included the 1987 Montreal Protocol on Substances that Deplete the Ozone Layer (UN, 1987)[1], the subsequent 1990 London Amendment (UNEP, 1990)[1], the 1992 Copenhagen Amendment (UNEP, 1992) and the 1997 Montreal Amendment. These agreements initially called for reduction of CFC consumption in developed countries [1]. A November 1992 meeting of the United Nations Environment Program held in Copenhagen resulted in substantial modifications to the protocol because of large observed decrease in ozone, and called for the phase-out of CFCs, carbon tetrachloride (CCl_4), and methyl chloroform (CH_3CCl_3) by 1996 in developed countries. As part of this, the USA, through the Clean Air Act (CAA), has eliminated production and import of these chemicals [5]. Production of these compounds is to be totally phased out in developing countries by 2006, while production of halons in developed countries was stopped in 1994. Human-related production and emissions of methyl bromide are not to increase after 1994 in developed countries, and should slowly decline with total elimination by 2005.

3- Methodology
Ozone depletion potential is a relative index to showing ability of ozone layer destruction of materials relative (CFC-11) and di-chloro-di-flouro- methane (CF_2Cl_2) or (CFC-12). These two substances have same destruction index and as ODE=1, these index depend on our current knowledge and may be revised periodically. UV-ray effects, number of halogens and carbon atoms in material and rate of dispersion in atmosphere are some important parameters that influence in ODP of materials. In a petrochemical complex, as a case study of research, some information forms about product characterization, production capacities, and personnel is gathered and expert team assessed process flow diagrams (PFDs). According to Montreal protocol, ozone

depletion substances (ODSs) that use in petrochemical complex, identified and research team focused on major usage and release of them in complex. With further studying of types of ODSs, five major categories found that usage of ODSs is possible in a petrochemical complex.

1-Fire fighting systems
2-Refrigerant packages
3-Used as extractors like solvents
4-Laboratory and analytical usage
5-Insulation purposes

Also in some special cases, ODSs uses as feedstock, and process materials, but they rarely happen in our case study. Technology and Economic Assessment Panel of Montreal Protocol researched on detection, identifying, and substitution technologies of these substances.
In many cases, taking suitable strategy of substitution, controls emission of ODSs to atmosphere, but in some cases unnecessary actions and without care substitution cause to emission of a large amount of ODSs to air. In these situations, management of exist system, and decrease alternate emissions is better than any substitution.
Halocarbons are one of the synthetic materials that introduced in 1960. Those ability to fire extinguishing and non conductivity cause to use large amount of these materials in fire fighting systems. Table 1 shows their application in some usual forms in petrochemical complex and their ozone depletion potential (ODPs) relative to tri-chloro-fluoro-methane ($CFCl_3$) or (CFC-11).

Table1- properties of halocarbons in usual forms

ODP	application	physical state in room temperature	chemical formula	commercial name
3	portable fire extinguisher	volatile liquid	CF_2BrCl	halon1211
10	static fire fighting systems	gas	CF_3Br	halon1301
6	fire fighting	volatile liquid	$C_2F_4Br_2$	halon2402

Some of suggested materials to substitution of halocarbons are: CO_2, inert gases, water mist, water, natural powders and fine aerosols and natural foams. Beside of these substances production and usage restrictions according to Montreal Protocol is on going firmly, some special usage like in aerospace, defense and oil and gas sector are going on.

4- Results

Iran is one of the members of The Vienna Convention for Protection of the Ozone Layer (1985) and The Montreal Protocol on Ozone Depletion Substances (1987). According to country commitment to decreasing and stopping ODSs, it can use financial aids to substitution of ODSs. Petrochemical complexes have potential of release of ODSs to atmosphere, thus in this research, a petrochemical plant is selected as a case study and because of their similarities results can extend to others.

4-1- Production and application of ODSs in petrochemical complexes

4-1-1- Refrigerant packages

According to filled forms by authorized personnel, only two substances from annex2 of Montreal Protocol use in fire fighting systems of plant. Table 2 shows their types and consumptions in some places of plant.

Table 2- ODSs in refrigeration packages

Year of operation	Refrigerant amount (Kg)	Type	No. of facilities	Section	Plant
1997	270	R-22	2	solvent recovery	polyethylene plant
1997	640	R-22	2	cooling of styrene	Tank farm
1996	86	R-22	2	N_2 production	N_2 plant
1997	100	R-22	1	cooling of styrene	storage tanks
1997	900	R-22	2	chilled water	polystyrene plant

4-1-2- Fire fighting systems

Based on filled forms by authorized personnel, two different systems (central and portable) of fire extinguishing facilities are used in complex. In both systems several types of substances are used. Table 3 shows types and consumption of them in some places of plant.

4-1-3- Solvents

According to annex2 of Montreal protocol, only carbon tetra-chloride (CCl_4) use in some cases that not specified usage location. Based on reporting of storage section, only 460 liters per year is purchased in last 3 years.

4-1-4- Laboratory and analytical usage

Because of high technological licensed equipments use in laboratories in plant, thus it doesn't find any document about the ODSs usage in laboratories.

4-1-5- Insulation

Insulation by poly-urethanes is under Montreal Protocol restriction. And only liquefied ethylene storage tank use this insulation in plant that contain tri-chloro-flouro-methane($CFCl_3$) or (CFC-11). But according to this subject that, this insulation is permanent and does not produce or reuse in other sections, this insulation isn't in ozone layer depletion activities.

5- Discussion

As mentioned above, only four ozone depletion substances are used in our case study as shown in table 4.

Substitution of three ODSs that have large amount of using, and according to type, amount and national characteristics of plant, two plans are applicable for emission decreasing:

1- Till 2010, application of above ODSs under suitable refrigeration management, and Halon management plan will continue, and plant have to start a plan for gathering, recycling, and gradually destruction of them under integrated management.

2- Direct action to change old technologies with new ones that adapt with ozone layer.

Table 3- ODSs in fire fighting systems

capsule No.	capsule capacity (Kg)	fire extinguisher mechanism	type of fire extinguisher	location
40	50	static	halon-1211	olefin plant
2	1000	static	chemical dry powder	polyethylene plant
1	2000	static	synthetic foam	polystyrene plant
54	40	static	CO_2	polyethylene plant
55	40	static	CO_2	polystyrene plant
20	50	static	CO_2	benzene plant
110	40	static	CO_2	power plant
300	6	portable	CO_2	distributed in site
300	12	portable	CO_2	distributed in site
300	30	portable	CO_2	distributed in site

Table4- ODSs and usage types in petrochemical complex

system	ODSs
refrigerant packages	R-12
refrigerant packages	R-22
fire fighting	Halon-1211
solvents	carbon tetra-chloride

5-1- Suggested substitutions

5-1-1-[R-12]

In order to saving money and other financial consequences, and according to point of view that ODP of R-12 is ten times higher than R-22 and with pay attention to this point that application (not production) of R-22 is permitted until 2040, it has suggested that R-22 is a suitable choice to substitution of R-12. Figure 1 shows R-12 substitution substances according to their ODP and effects on global warning.

As shown in figure 1 , and in temporary section R-22 that now use in plant is a alternative to R-12 , but according to its restriction by Montreal Protocol, it is better that use another substances to substitution of R-12.

In permanent section, non-halogenated materials like NH_3 and iso-butane (R-600a) and propane (R-290) is good choices because of their zero ozone depletion potential. But their usage facilities are big and non-economical to substitution (not installation), specially in our case (because of changing in many equipments). Thus, in second group (HFCs) the most applicable and efficient for our purpose and suggested in many cases is R-134a (1, 1, 1, 2, tetra-fluoro-ethane) or (CH2FCF3).

5-1-2- Temporary substitutes

Chlorinated materials with low ODPs are one of choices for substitution of ODSs because low their possibility to use until 2040 under Montreal Protocol. According to low cost of substitution and applicability in many countries, retrofitting with HCFC is a transitional path and must be with care and precision.

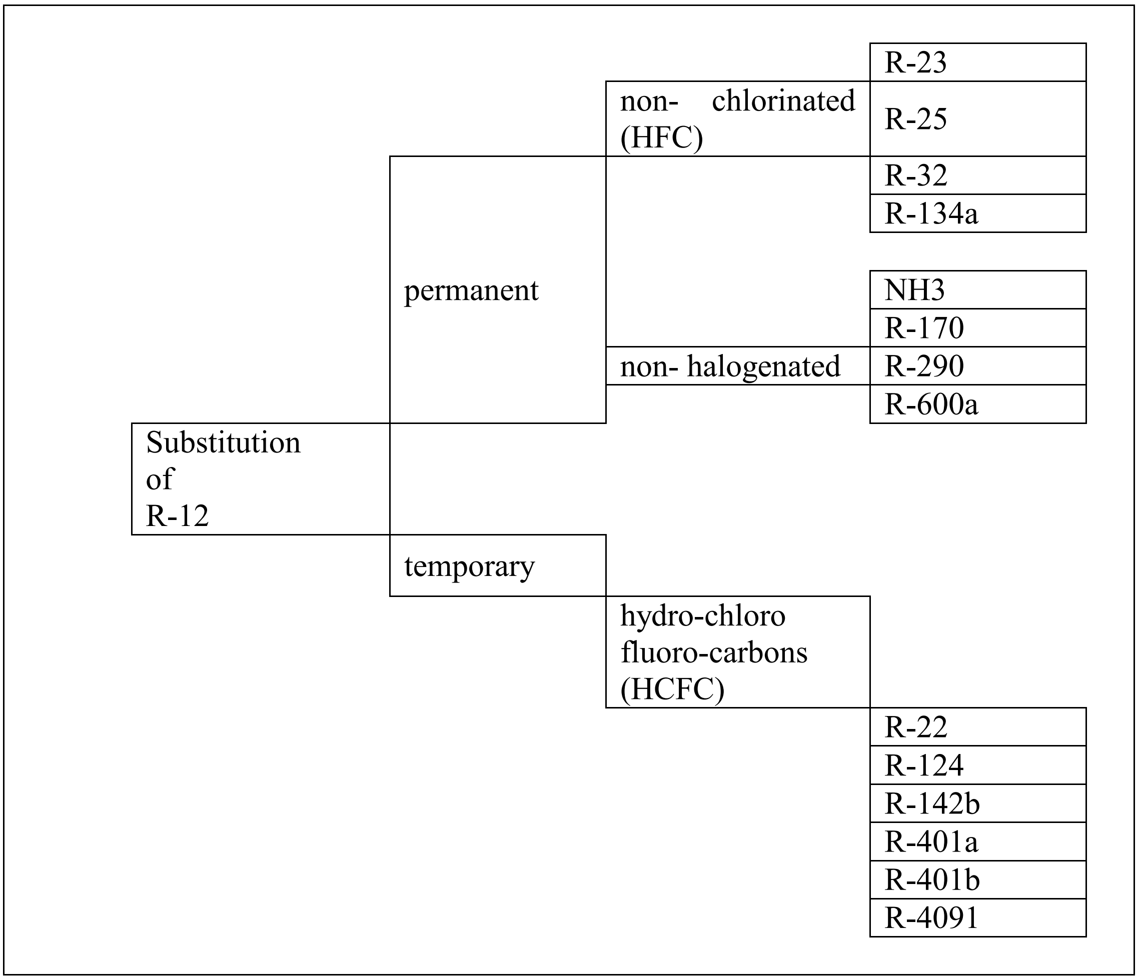

Figure1- substituted substances for R-12

5-1-3-Permanent substitutes

Non-halogenated substances and hydrocarbons with zero ODPs are a alternates of R-12 substitution. Beside their environmental friendly properties, their flammability, and system maintenance, are two major problem of their commercial scale application in many countries.

Also because of their low refrigeration capacity (about half of R-12), bigger compressors must be used to give same operation.

According to production of hydrocarbon gases like butane and propane in petrochemical industries, it is possible to think on them as good substitution of other refrigerants.

6- Conclusion

According to previous researches and our prediction in a petrochemical complex, results show that only three major ODSs are used in plant, R-12, R-22, and Halon1211. By further focus on application of these materials and possible substitutes according to availability, cost and applicability, R-22 and R-134a consider as good alternates of R-12, first as temporary plan and second as permanent. Also, CO_2 select as good choice of substitution of halon1211, because of its fire fighting purposes. Now Halon1211 substitution with CO2 is done and R-12 substitution with R-22(in some cases) as temporary plan are doing and use of R-134a as permanent substitutes and start a feasibility study of changing R-12 with Hydrocarbons like iso-butane and propane as refrigerants in next five years in all petrochemical complexes nationwide.

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