

Should Halons be Destroyed or Converted to Other Chemicals?

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This paper addresses the concerns related to the stockpiled halons, such as 1301 (CBrF_3) or 1211 (CBrClF_2) fire suppressants, which have been accumulated by various western governmental organisations, in order to provide uninterrupted supply of halons for critical uses. Halons are no longer manufactured in industrialised countries and their production in developing countries will soon come to an end. Halon-replacement and substitute fire-suppression technologies have been developed and are now widely accepted. For this reason, it appears that there is no need for the continuing existence of large national halon banks.

If halons were to be banned and pronounced waste materials by an international agreement similar in nature to the Montreal Protocol (which provided the timetable for halon phase-out but did not ban these chemicals), implementation of halon elimination processes will need to be carried out. Two groups of technologies have been developed for handling halons: (i) those that *destroy* the valuable C-F bond, usually by heating halons to very high temperature and (ii) those that attempt to preserve C-F bond by *converting* halons to other useful chemical.

The Australian experience indicates that the destruction technologies can only be implemented if supported by substantial government funding or by compulsory surrender fees charged to halon users. In the latter case, limited compliance would be expected if a forced halon surrender program were to be implemented around the world. The problem is obviously linked to the inherent drawback of halon destruction technologies, including the Australian thermal-arc plasma, of being unprofitable and therefore unable to operate without subsidies. This is not the case for halon conversion technologies, which offer the potential of halon elimination by processing them to other chemicals, minimising costs to be borne by governments and halon users. The paper also reviews the technical and economic details of the most promising halon-conversion technologies.

INTRODUCTION

Halons are brominated fluorocarbons or brominated chlorofluorocarbons. They include the following chemicals which were, and in some countries still are, used in fire suppression applications:

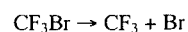
CF₃Br: halon 1301, bromotrifluoromethane, IUPAC formula: CBrF₃

CF₂ClBr: halon 1211, bromochlorodifluoromethane, IUPAC formula: CBrClF₂

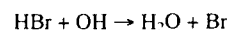
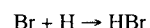
C₂F₄Br₂: halon 2402, dibromotetrafluoroethane, IUPAC formula: C₂Br₂F₄

CF₂Br₂: halon 1202, dibromodifluoromethane, IUPAC formula: CBr₂F₂

At high temperature in flames, halons quickly decompose to produce Br radicals, for example in the case of CF₃Br:



Subsequently, bromine radicals remove chain propagating hydrogen radicals in flames along the following catalytic cycle,



Note that the bromine radical is regenerated in the flames, and can facilitate the removal of a large number of hydrogen and hydroxy radicals. For completeness, we mention that the CF₃ radical can enter the hydrogen removal reactions, but the removal pathway is not catalytic and leads to the formation of hydrogen fluoride, a very toxic gas. This occurs along the following kinetic pathway:



The removal of H to HF is of negligible importance in halon mitigated flames. However, it is worth pointing out that hydrofluorocarbons, which have been introduced to replace halons in some applications, rely on very good cooling properties in extinguishing fires, but they also display small chemical effect of removing hydrogen radicals via the route to HF. Unfortunately, this results in the production of substantial amounts of HF, often in excess of 3000 ppm, in flames suppressed with hydrofluorocarbons. In comparison, the levels of HF in halon mitigated fires are usually in the order of 300 ppm or less.

In addition to their excellent suppression characteristics due to the removal of hydrogen radicals, halons are also very good coolants; that is their thermal capacity is high. Several phenomenological schemes have been developed to gauge the relative importance of the chemical and physical modes of suppression. One such scheme, proposed by Dlugogorski et al (1996), is based on considering the extinguishment process to be reflected by the parallel action of heat extraction and chemical reaction. This leads to the results presented in Table 1, which were calculated from cup burner data. Observe that for halons $R^{\text{heat}}/R^{\text{chem}} > 8$, for hydrofluorocarbons and hydrochlorofluorocarbons $R^{\text{heat}}/R^{\text{chem}} \approx 1.1-1.2$, and weak chemically active suppressants possess $R^{\text{heat}}/R^{\text{chem}}$ of below 0.4. It should be appreciated that the physical and chemical extinguishment mechanisms are intimately coupled, that is as the temperature changes due to cooling and so do the kinetic rates. This means that simple schemes as the one just mentioned are very approximate in their nature.

Table 1. Relative importance of chemical and physical action for some selected agents. Extinction and heat capacity data were taken from Heinonen and Tapscott (1995).

Agent	Cup burner % (Total resistance, R^{tot})	Cooling resistance, R^{heat}	Chemical resistance, R^{chem}	Relative importance, $R^{\text{heat}}/R^{\text{chem}}$
CF ₃ Br	2.9	26.8	3.3	8.2
CHCl ₂ CF ₃	7.1	15.7	13.0	1.2
C ₂ HF ₇	6.3	13.1	12.2	1.1
CF ₃ I	13.8	18.3	56.3	0.3

Unfortunately halons, like CFCs, have very long tropospheric lifetimes, and consequently can diffuse into the stratosphere. In the stratosphere, halons and CFCs are broken down by UV light, resulting in formation of Cl and Br radicals, which catalyse the depletion of the ozone layer, the earth's primary shield against harmful UV radiation (Molina and Rowland, 1974). It is estimated that one molecule of chlorine can decompose over 100,000 molecules of ozone molecules before being removed (Garcia and Solomon, 1994; Solomon et al, 1995). In fact, Br radicals are suggested to be 10-100 times as destructive as chlorine atoms on a per-atom basis (McElroy and Salawich, 1989).

The Vienna Agreement in 1985, followed by the Montreal Protocol in 1987 with its later amendments, especially in Copenhagen and London mandated the phase out of halons in industrialised countries by Dec 1993. The Protocol has also allowed the production of halons to continue in developing countries, so called Article 5 countries. It has allowed halon production for critical applications. As far as we know, this provision has not been taken up by any industrialised nations. Finally, parties of the Protocol were allowed to impose more stringent controls of halons. Subsequently, Australia, Denmark, Germany and Sweden introduced bans on halon use in addition to ban on halon manufacture. In European Union such additional restrictions were allowed as long as they did not interfere with free trade.

Considering the fact that halon released anywhere in the world eventually migrate to the ozone layer above Antarctic, halons deserve to be included in the list of trans-national pollutants. Most cases regulated by the Montreal Protocol have shown a significant decrease in their net emission rates, although exceptionally the emission of halon 1211 has remained rather constant (Butler et al, 1998; Fraser et al, 1999). Indeed, use of halon 1211 is still permitted, but only for specific, mission critical applications such as aviation protection and rescue operations. This suggests that halon 1211's emissions continue in spite of the ban on its production, as well as the general availability and acceptance of halon 1211 alternatives (UNEP Technology, 1998). With its current emission rate, halon 1211 poses a more significant ozone destruction capability than any other halocarbon (Montzka et al, 1999).

Since the time when the ozone depleting characteristics of halons become evident, new fire suppression technologies have been developed. For most part, they are not as versatile and effective and those based on halons. The new technologies require more careful engineering, cost more to test and are not as forgiving as the halon based systems. Those technologies include inert gases (CO₂, N₂, gas mixtures), clean agents (hydrofluorocarbons, perfluorocarbons, hydrochlorofluorocarbons, and CF₃I which is as effective as halons themselves), water mists, foams (especially, compressed air foams), aerosols and powders. No doubt that some of these agents have their own problems: For example, PFCs have high global warming potential and HCFCs have small ozone depleting potential. On the other hand, the initial concerns about CF₃I appear to have been unjustified (Newcastle, 2001). This means that, from a technological perspective, all halon applications can now be replaced with one or several new suppression technologies.

It is clear that there exists substantial opposition against converting halons, with three arguments usually cited: (i) The existing military application require halons. In our view, all military applications of halons can now be converted to other technologies. However, the bona fide issues involve finding additional storage space, increase risks as well as time and expense for converting to new fire suppression technologies (Liddy and Moore, 2000). (ii) Losses in decommissioning, handling and transport could accelerate the growth of the Antarctic ozone hole (Ball and McCulloch, 2000). These effects could be minimised by training and monetary incentives, especially halon conversion technologies are operated profitably (that is they produce saleable chemicals), allowing funds to be used for purchasing halon waste. (iii) Once the halons are disposed, governments could be embarrassed for applying for essential production permit. For this to eventuate, there would have to be a future application for halons that could not be replaced with an alternative fire suppression technology. However, past experience indicates that given time and resources new technologies are always developed.

The removal of halons from use has resulted in two problems: one related to the need to treat the growing stockpiles of halons, and the second related to the need of developing suitable replacements for these compounds. The current focus of worldwide research is on the development of treatment technologies for halons, where destruction and conversion are parallel alternative treatment approaches. In this paper we argue that halons should not be considered waste material in the traditional sense of this word and must not be destroyed. Rather they should be thought of as valuable chemical feedstocks which could be converted to other chemicals.

ISSUES RELATED TO HALON COLLECTION

Any process designed to destruct or convert halons to useful chemicals in an economically viable and environmentally sound fashion needs to rely on large amount of stockpiled material. Until present, the efforts to create large halon banks have been driven either by a strong political will, as is the case in Australia, or by the necessity of ensuring a reliable source of supply of halons to military users, as exemplified by the USA. Engendered by the legislation, the Australian approach called for the removal and collection of halons and CFCs by the fire-protection and refrigeration industries. These industries were then required to surrender halons and CFCs to the Australian halon bank together with a disposal fee. The collection process involved an awareness campaign and volunteer work, including members of the Fire Protection Association Australia. In contrast, the approach taken in the USA was to operate in the existing market place by offering a competitive price for halons.

If halons were to be banned and pronounced to be waste materials by an international agreement similar in nature to the Montreal Protocol (which provided the timetable for halon phase-out but did not ban these chemicals), an implementation of halon elimination processes will need to be carried out in conjunction with the collection of these chemicals. The cost of halon removal from existing fire-protection systems and the usual confined success of public awareness campaigns for the collection of hand-held extinguishers would very likely result in limited compliance with a collection program involving surrender fees. At this point, it is instructive to examine the Australian experience in banning, collecting and destroying halons and CFCs, an initiative, which as yet has not been followed by majority of industrialised countries. The Australian stance is easy to understand in light of the growing Antarctic ozone hole and the increasing exposure of the Australian population to UV radiation. Historically, this population has had very high incidence of skin cancer, about four times as high as is the case for the rest of the world.

The Australian experience seems to indicate that about 50% of the existing halons has been surrendered as a consequence of a fee-based collection program¹. The problem is obviously linked to the inherent drawback of halon destruction technologies, including the Australian thermal-arc plasma, of being unprofitable and therefore unable to be operated without a financial support of national governments. In Australia, the cost of halon destruction was shifted from the government to halon and CFC users by legislative measures. One can foresee a comparable result, if a fee-based user-paid collection program is implemented in other industrialised countries. In addition, the developing countries would be unable to finance collection programs themselves, necessitating international support for that purpose.

In our view, the destruction of halons can be fully successful only if supported by substantial funding from governments in industrialised countries. The funding would need to cover purchasing halon from users, including those in developing countries, and paying for halon destruction. This is not the case for halon conversion technologies, which offer the potential for halon elimination by processing them to other chemicals, minimising costs to be borne by governments and halon users. From this standpoint, banning of halons may lead to the emergence of several halon conversion processors vying for collecting and disposing available halons, without government intervention. This opens a possibility for halon processors actually paying for halon feedstocks, offsetting halon removal costs from fire-protection systems. Small quantities of impure or contaminated halons could be destroyed in the existing incineration facilities, such as those handling PCB-contaminated materials.

RECENT DEVELOPMENTS ON HALON CONTROLS

The issues discussed briefly in the section are in the state of flux, with more developments likely to become public by the time this paper is published. In the USA, the Department of Defense has established a cleaning up and recycling program for re-use of halons in critical military applications, with the critical use reviewed monthly by each service (that is Army, Navy and Air Force). Likely throughput is above 5,000 T/y (Sibley, 2000; personal communication). Collection facilities have been established in Germany, Japan and the USA with additional acquisition from custom seizures, and overseas purchases, including the purchase of 250 T of CF₃Br from the Australian government. In addition, the so called Clinton's "Green Government" Executive Order of April 2000 stipulated reduction in use of ozone depleting substances, with all agencies required to stop using them by 2010. It appears that the USA will not embark on banning the use of halons in the near future. Though, the established halon bank in the USA could provide a consolidated source of halon for disposal purposes, if there is a change in the policy.

In the 15 member states of the European Union, the present regulation banned the *production* of halons a year before the phase out deadline of the Montreal Protocol. The new regulation will ban the *use* of halons by 2002 and enforce decommissioning of halon systems by the end of 2003. The agreement on the new regulation will probably be reached by June 2000. The most important part of the regulation is Annex VII which lists critical uses of halon 1301 in aircraft, military, petrochemical, Channel tunnel and critical uses of halon 1211. However, at present changes are still being made to the annex (Liddy and Moore, 2000).

¹ Though, it has been suggested that the amount of halons actually available for collection was well below the initial estimate.

HALON DESTRUCTION TECHNOLOGIES

Generally, there are two options for halon treatment: destruction and conversion. Destruction aims to transform halons into environmentally benign species. Currently available halon destruction technology include incineration and pyrolysis. Incineration converts halons into carbon dioxide, water and hydrogen halides (HCl, HF and HBr) through high-temperature decomposition. However, the disadvantages of incineration, such as high-energy costs, generation of toxic chemicals and products of incomplete combustion (PICs), make it a generally unattractive treatment option. Plasma arc pyrolysis processes, a relatively new technology, has been commercialised in Australia. It utilises high temperatures to pyrolyse halons into atomic and ionic species. Subsequent, down stream treatment converts these species into environmentally benign products such as mineral salts, H₂O and CO₂ (SRLPLASMA Limited, Victoria 3136, Australia). However, the operating cost of this process is 3-5 times the operating of conventional thermal incineration (Dickerman et al, 1989).

This section reviews the available technologies for destruction of halons and is based on the summary prepared by Andrews et al (1996). In general, these processes fail to take an advantage of halons as feedstock to other materials, by processing halons to fluorinated solvents, refrigerants or blowing agents. Rather the focus is on decomposing halon molecules to materials which do not preserve carbon-fluorine bonds, and therefore have little or no economic value. This makes them unprofitable and unable to operate without direct subsidies or surrender fees.

Incineration

Concentrated organic wastes are presently being destroyed primarily by incineration in rotary kilns, gas fired chambers, fixed-hearth incinerators and circulating bed combustors. Because incineration destroys wastes by burning them in air or oxygen, it has a number of significant disadvantages, including auxiliary fuel requirements, formation of NO_x and toxic products of incomplete combustion, material incompatibility problems (with halogens), and large dilute effluent volumes. Incinerators also must be equipped with secondary combustion chambers and stack gas clean up devices to achieve mandated destruction and removal efficiencies. The incineration costs tend to be high (Surprenant et al, 1988).

Molten Glass Incineration

Molten glass incinerators are electric furnace reactors in which a pool of molten glass is used to destroy hazardous organic wastes and/or to encapsulate solid by-products of hazardous waste treatment (Surprenant et al, 1988). The process is regarded highly for the destruction of highly toxic organic wastes and contaminated soils. The system is considered to have technological and economic advantages over other established incineration technologies (Surprenant et al, 1988). However, problems in disposing the waste product material in landfills cause some major concerns. Additionally, no data demonstrating destruction of halogenated wastes was found in literature, limiting the possible scope of this technology to destroy halons.

Molten Salt Destruction

Molten salt incineration involves the combustion of waste materials in a bed of molten salt (Na₂CO₃). The bed is maintained at temperatures of 800-1000°C. The waste is fed in and reacts to form inorganic salts retained in the melt (Surprenant et al, 1988). Molten salt destruction systems are limited to the incineration of hazardous wastes which have a relatively low percentage of solids

or inorganics. Molten salt is also corrosive increasing the cost of destruction. Molten salt incineration has been shown to destroy PCBs (Surprenant et al, 1988). Although the technology could be applied to halon destruction, we have been unable to locate relevant publications.

Plasma Arc Pyrolysis

Plasma is an ionised gas consisting of molecules, atoms, ions and electrons and is electrically conducting. Gases become electrically conducting at 4000°C, with industrial plasma systems operating at approximately 10,000°C (Hawkes and Frost, 1995). A plasma column is generated by the passage of an electric current through a gaseous medium between a cathode and an anode. At the centre of the column, temperatures of up to 20,000°C can be attained. The use of plasma has been limited by characteristics of the technology, including limited scale up capability, low thermal efficiency and limitations in electrode design (Hawkes and Frost, 1995). Electric arc plasma offers the advantage of very high temperature, high energy density and accurate rapid control of the process. At present three plasma technologies are available, although only the Plascon process is used commercially for halon destruction:

Electricite de France Process

This process utilises a non transferable arc plasma coupled to a furnace that accepts both solid and liquid wastes. Molten material is tapped to produce vitrified material ingots and acids are quenched and scrubbed with caustic. The plasma gas may reach 10,000°C but the furnace operates at only 1,500°C. This furnace temperature is within the range of current incinerators (Hawkes and Frost, 1995).

Plasmox Process

Plasmox was originally applied to metallurgical processes but has now been developed to fully integrated waste treatment. The principal feature of this device is a rotating pyrolysis chamber that creates enough force to move the molten waste material to the outer circumference chamber. The molten material and gases are then further processed by another plasma arc. The molten material is again produced as a vitrified slag and the gas is then quenched and scrubbed (Hawkes and Frost, 1995).

Plascon Process

This plasma process, unlike the other two processes, operates in a continuous rather than in batch fashion. Plascon offers a high destruction performance of a wide range of materials and a suppression of back reactions that produce toxic by-products. The process includes rapid heating of the waste, pyrolysis with plasma in an argon inert environment and rapid quenching. Off gases are flared to a packed column for conversion of CO and H₂ to CO₂ and H₂O (Hawkes and Frost, 1995).

Wet Air Oxidation

The oxidation of suspended and dissolved contaminants in aqueous waste streams is known as wet air oxidation (WAO) (Surprenant et al, 1988). Operation is carried out at elevated temperatures and pressures achieving acceptable reduction in contaminant levels. The WAO process is available

commercially, and is used predominantly as a pretreatment step to enhance biodegradability in treating municipal and industrial sludges. Other physical forms of wastes treatable by WAO are not defined in the literature but it appears that the process can be used for oxidation of halogenated wastes, as long as they are dilute but too toxic for biological treatment. Limitations associated with the use of WAO begin with expensive construction materials and design features. Installed capital cost for WAO is 50% higher than that for incineration (Surprenant et al, 1988). The presence of residuals in both the vapour and liquid phases, which may require additional treatment, is considered unfavourable. Also many halogenated compounds are resistant to wet air oxidation and cautious consideration should be given in its application as a pretreatment method for halons.

Steam Reforming

Steam reforming is the reaction of organic compounds with superheated steam, and is widely used in industry (Nimitz, 1991). For example, methane is reformed with carbon dioxide producing carbon monoxide and hydrogen. Since reforming is not a combustion process, no fuel, air, or oxygen need to be supplied to the reactor. In contrast to incineration, destruction of organic chemicals by high temperature, solar-driven catalytic steam reforming produces no incomplete combustion products or NO_x . The Soltox process describes an attractive alternative to incineration of liquid and gaseous organic wastes (Tyner, 1990). The solar catalytic destruction of organics by steam reforming appears well suited for haloalkanes including CFCs and halons. The Soltox process involves the destruction of gaseous and liquid wastes by steam reforming over a rhodium metal catalysts supported on a porous ceramic absorber and heated to high temperatures by concentrated solar energy (Tyner, 1990; Nimitz, 1991). The Soltox system should have a wide acceptance because the reforming reactions are inherently cleaner than incineration. The system can operate on the waste generating site avoiding hauling and other associated costs.

Supercritical Water Oxidation

Supercritical water (SCW) oxidation is an oxidation process carried out in a water medium at supercritical temperature and pressure (Surprenant et al, 1988). It is a technology proposed for the destruction of organic containing wastes. In the supercritical region, oxygen and organic compounds become totally miscible with the SCW and inorganic compounds become sparingly soluble. When combined in the SCW process, the organic materials oxidise and inorganic salts are precipitated by the supercritical water. The cost of oxygen consumed in the process is the most significant operating cost (Surprenant et al, 1988). Potential limitations of the process relate to the cost and equipment limitations due to stringent temperature and pressure requirements. CFCs have been studied and were shown to decompose at temperatures between 400 and 600°C (Nimitz, 1991). We stress that the development of SCW oxidation is in its infancy and no data exist in relation to the disposal of halons.

UV/Ozonation

The development of a destruction technology involving a photocatalytic process capable of detoxification of industrial organic waste water has been identified (Tyner, 1990). The unique characteristics of solar energy plays an important role in this process. The contaminated water flows through a reactor onto which sunlight is focussed. UV energy is absorbed by and activates a catalyst (titanium dioxide) in the waste stream. A reaction with added oxidants (eg hydrogen peroxide) occurs forming reactive oxidisers, which in turn attack organic molecules. This process can destroy most halogenated organic compounds, including solvents, PCBs and dioxins. Capital

and operating costs depend on the concentration of oxidisable species in the waste stream. If concentration levels remain low, in the order of 1%, then the operational costs remain minimal. However, fully halogenated compounds such as carbon tetrachloride are uniquely resistant to attack (Tyner, 1990). Thus the process is not likely to have potential for application to destroy halons used in fire fighting. Ozonation is particularly suited for treating industrial waste containing low levels of toxic organic contaminants (Surprenant et al, 1988; Tyner, 1990; Nimitz, 1991). Handling of more concentrated waste would result in a drastic increase in costs (Surprenant et al, 1988).

Biological Destruction

Biological treatment involves the destruction of organic compounds by microorganisms. Conventional biological treatment methods include trickling filters, activated sludge, aerobic and anaerobic digestion and composting (Surprenant et al, 1988). Conventionally, the process is used to treat aqueous wastes containing biodegradable organic compounds. Complete biological destruction is not very common, as many compounds are not readily degraded by naturally occurring microorganisms. This process is still in the developmental stage and relevant literature is scarce. Halogen compounds in the literature are biologically difficult to degrade.

Hydrolysis

Finally we would like to comment on the hydrolysis of haloalkanes. In general, the rate of hydrolysis depends on the nature of haloalkanes. In the particular case of halon 1301, it was found that the hydroxide ion is unreactive towards CF_3Br (Stanecke et al, 1995). Thus this technology cannot be used for destruction of halons used for fire mitigation.

HALON TO USEFUL PRODUCTS CONVERSION TECHNOLOGIES

In many respects, the conversion of halons and CFCs into valuable chemicals would be a preferred option to destruction process (Kennedy et al, 1997; Wiersma et al, 1998). As this section demonstrates, technologies exist that operate on the principle of cleaving the C-Cl and C-Br bonds and preserving the valuable C-F bonds. This means that from halons as feedstocks one can obtain fluorocarbon and hydrofluorocarbon products. Large stockpiles of halons in halon banks are now available allowing the design and operation of larger scale conversion processes, which would take advantage of the economy of scale.

Non-oxidative Thermal Hydrodehalogenation

Non-oxidative thermal hydrodehalogenation (THD), where halons or halogenated compounds react with hydrogen or hydrogen donors at high temperatures, is one of such emerging treatment processes. de Lijser et al (1994) have investigated THD of bromochlorodifluoromethane (halon 1211) in hydrogen, and have found that at low temperatures, below 873 K, the reaction products were direct hydrogenation species such as CHBrF_2 , CHClF_2 and CH_2F_2 . With increasing temperature, production of the defluorination product, CH_4 , increases. These results suggest that the reaction process is initiated by rupture of the C-Br in CBrClF_2 , followed by hydrogenation of CClF_2 to form CHClF_2 .

de Lijser et al (1994) proposed that CHBrF_2 is produced via the combination of HBr and CF_2 , which, in turn, was formed from the decomposition of CHClF_2 through elimination of HCl . Byproduct species CH_2F_2 and CH_4 are considered to form via abstraction of bromine, chlorine and

fluorine from CHClF_2 , CHBrF_2 and CHF_2Cl by H_2 , followed by hydrogenation. This mechanism is generally consistent with that suggested by Ritter (1994), who studied 1,1,2-trichlorotrifluoroethane ($\text{CCl}_2\text{FC}(\text{Cl})\text{F}_2$, CFC 113) decomposition in H_2 over the temperature range of 923-1098 K and at a residence time of 2 s. In Ritter's investigation, the onset of defluorination temperature occurs at 973 K, which is 100 K higher than that observed by de Lijser et al (1994).

The reaction of CBrF_3 with H_2 in a shock tube was investigated at 1000-1600 K and 1.2-2.6 atm by Hidaka et al (1993). However, these researchers did not observe any evidence of defluorination under any conditions, and only detected CHF_3 , C_2F_6 , C_2F_4 and HBr as reaction products. In their 14 step reaction mechanisms, no defluorination products, such as CH_2F_2 , were taken into account. Recently, we reported the results of studies on the hydrodehalogenation of CBrF_3 with hydrogen between 673 and 1073 K at ambient pressure, where CHF_3 was found to be the primary reaction product (Li et al, 2000). We also analysed the reaction mechanism and found the attack of H radical on CBrF_3 to produce CF_3 and HBr is the major elemental reaction leading to consumption of CBrF_3 .

Our work at the University of Newcastle focuses mostly on the design of hydrodehalogenation based processes. An overview of one of such processes is presented in Figure 1 and a more detailed flowsheet is illustrated in Figure 2 (Andrews et al, 1996). The process involves the reaction of halons in a fluidised bed and the separation of the acid and hydrocarbon products of reaction. The halons are reacted in excess hydrogen at 850°C and 1 MPa for 2.5 s. One can replace H_2 with methane as a cheap source of hydrogen.

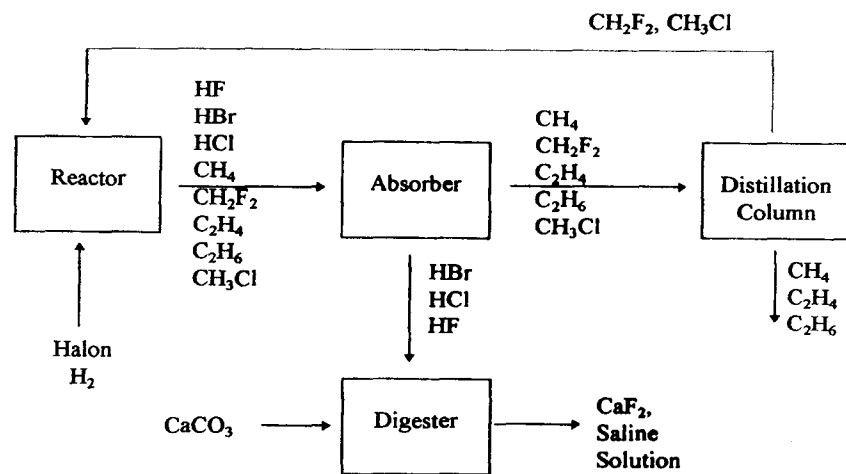


Figure 1. A block diagram of a typical hydrodehalogenation process.

The mineral acids are removed from the product stream by absorption with water in the absorbers. The acid solution is reacted with calcium carbonate to yield mineral salts. The remaining components in the reactor product stream are then compressed in order to separate hydrogen. The partially reacted halogenated compounds are separated from the hydrocarbon fuel components in the distillation column and return to the reactor.

The reactor is a vertical gas phase non catalytic fluidised bed reactor operating under isothermal conditions at 840°C and 10 bar. Due to the extremely corrosive environment, the internals of the reactor are cast from alumina refractory. The reactor walls are surrounded by a thermally insulated layer to minimise heat losses and maintain the temperature above the dewpoint of the three mineral acids. The exterior of the reactor is a welded carbon steel jacket fitted with access manholes for maintenance, a distribution box and a distribution plate consisting of nickel-chromium-molybdenum alloy. The vessel volume is approximately 1 m³ with a height of 2.5 m.

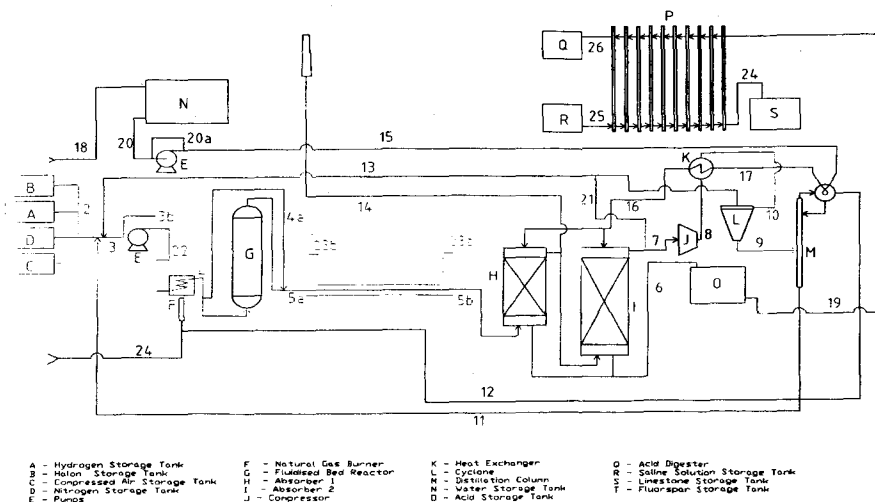


Figure 2. Flowsheet for the hydrodehalogenation process for treating halons 1301 and 1211 developed at the University of Newcastle.

The acid absorption system comprises two absorbers in series following the reactor. Due to the high temperature and corrosive environment, the first absorber consists of a fibreglass reinforced polyester with refractory lining of a fusion cast of alumina refractory brick. The second absorber is made of vinyl esters. Vinyl esters are easily moulded and are sufficiently strong to support the weight of the absorber and its contents. The flowrate of water through the absorber is about 1500 L/h to ensure complete absorption of the three mineral acids produced in the reaction process. The efficient operation of the absorption system is vital to protect all downstream unit operations from the extremely corrosive properties of hydrofluoric acid.

The digesters react limestone with mineral acids by producing dissolved salts including calcium fluoride, which has commercial value. The digester consists of ten 4 m columns connected in series. The columns are made from polyvinyl chloride which is inexpensive and resistant to hydrofluoric acid attack.

The aim of the distillation column is to separate unreacted components from the product stream back into the reaction process. These include intermediate chlorofluorocarbons such as difluoromethane and methyl chloride. The column is 0.3 m in diameter and is 3 m tall, with 11 evenly spaced bubble cup trays. The column operates at a pressure of 17 MPa using cooling water

to recondense vapour. To ensure minimal corrosion and maximum strength, required when operating at high pressures, 302 stainless steel needs to be used for column construction.

In summary, the presented hydrodehalogenation process requires much lower setup and operating costs compared with plasma-based systems. It uses a non oxidative reaction technology and is not specific, that is it can treat all halons. For the process illustrated in Figure 2, products generated in the process are of minor economic value. This should not be seen, however, as a drawback of the hydrodehalogenation processes in general. One can design specific processes that selectively convert halons 1301 or 1211 to specific hydrofluorocarbons. As an example, we cite our latest process for conversion of halon 1211 to $C_2H_2F_2$, a valuable feedstock (Tran et al, 2001).

Furthermore, we have studied the nonoxidative gas phase reactions of halon 1311 with methane in a tubular plug flow alumina reactor at atmospheric pressure and residence times between 0.1 and 1.3 s (Tran et al, 2001). With an equimolar feed of $CBrClF_2$ and CH_4 , complete halon conversion was achieved at 1073 K for all residence times considered. The initial products of the reaction were $CHClF_2$ and CH_3Br , which were replaced by $C_2H_2F_2$ at elevated temperatures.

Another possibility is to convert CF_3Br to CHF_3 by reacting halon 1301 with methane (Li et al, 1999) followed by the conversion of CHF_3 to CF_3I (Nagasaki et al, 2000). The flowsheet of the process is similar to that presented in Figure 2 and to the pyrolysis process described in the next section. The conversion of halon 1301 to CHF_3 can be operated either catalytically or non catalytically. The strengths of the process include high-valued products with methane available at low cost, good product selectivity achieved in non oxidative reaction environment. The drawback of the process lies in its separation. The process of Nagasaki and his coworkers relies on the catalytic reaction of CHF_3 with I_2 in the presence of oxygen to ensure favourable thermodynamic driving force. It appears that in the presence of porous carbon is also necessary, for thermodynamic reasons, although Nagasaki et al explain the need for porous carbon on kinetic ground to increase the activity of their catalysts.

Pyrolysis

The flowsheet for this process is illustrated in Figure 3. The primary components of this process are halon purification stage, the conversion reactor and finally the separation stages. The purification stage involves the removal of unwanted contaminants from the collected halons. Impure halon contaminated with nitrogen and water is decanted from containers to a collective storage unit where it is passed through a molecular sieve filter to remove the water. Once the water is removed, the halon is passed to the reactor where it is thermally converted to hexafluoroethane, C_2F_6 , and bromine at temperature of 1200 K and near atmospheric pressure at a residence time of 1-2 s. The nitrogen flows through unreacted (Potter et al, 1998).

The bromine component is removed in the blowdown tank, and is sent to a storage facility. Any remaining bromine is separated from other components in an adsorption column. The next step includes the separation of C_2F_6 , N_2 and unconverted $CBrF_3$ in a cryogenic distillation column. $CBrF_3$ is recycled back to the reactor, while C_2F_6 and N_2 which come off the top of the distillation column are first fed to a recovery tank to recover the majority of the product, then sent to remove trace amounts of C_2F_6 remaining in the nitrogen waste stream.

In summary, this process is specific only to converting halon 1301 to C_2F_6 and cannot be used for treating halon 1211. Its advantages are production of valuable products, almost exclusively C_2F_6 with few minor products. This translates into simplified separation and purification unit operations.

Also, the reaction is carried in non oxidative environment, avoiding production of toxic combustion byproducts.

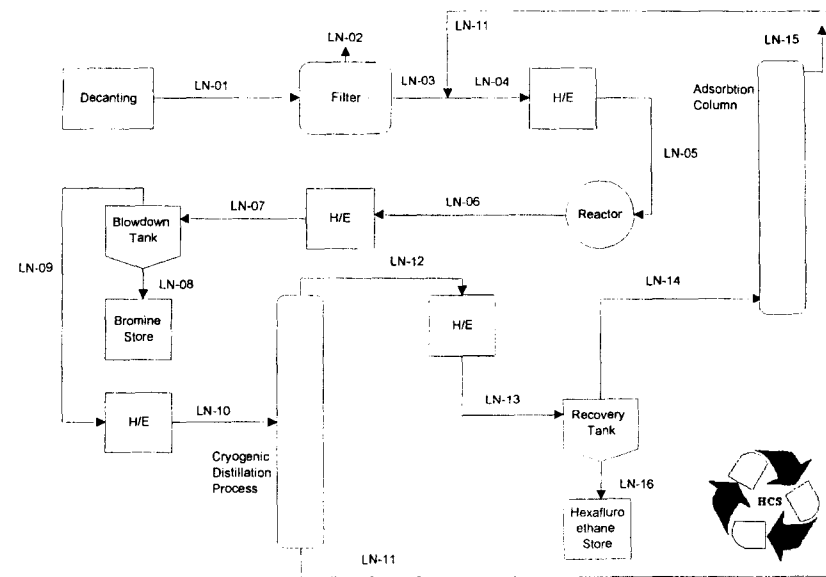


Figure 1 Process flowsheet

Figure 3. Flowsheet for a process of pyrolysis of halon 1301.

In addition to the two step conversion of CF_3Br to CF_3I described earlier in the paper, there exists an electrochemical process for direct conversion of halon 1301 to CF_3I , with its flowsheet illustrated in Figure 4 (Edwards et al, 1997). The process itself occurs within a solvent, in two separate stages (Naumann et al, 1990). The solvent employed is known as dimethylformamide (DMF). It is a powerful, yet common industrial solvent which has a unique combination of physical properties, ideal for the process.

The first stage of the process involves an electrochemical reaction in which halon 1301 is bubbled over a platinum cathode to form two anions (CF_3^- and Br^-). These two anions subsequently react in a remarkably selective fashion with zinc cations to form an organometallic resin compound, CF_3ZnBr . This compound is quite insoluble in most solvents except for DMF and other related substances. The DMF is unaffected by the conditions in the cell.

Upon leaving the electrochemical cell the CF_3ZnBr/DMF solution passes through a filtration step to remove any particulates of zinc and any other solid impurities. It then enters the second stage of the process. In the second stage the CF_3ZnBr/DMF solution is mixed with monobromide iodine (Ibr) in a series of four water cooled tank reactors. An exothermic reaction ensues from which the desired trifluoroiodomethane evolves. CF_3I is unaffected by the solvent and immediately escapes from the solution. In this stage the DMF acts as a heat sink for the reaction whilst also being able to dissolve the monobromide iodine. A large proportion of the heat released in the reaction is taken up by the DMF. Cooling is, however, still needed. The role of the solvent is also to dilute the participating

species, CF_3ZnBr and IBr . Reacting them in a concentrated form will lead to a near explosive conditions and quite uncontrollable reaction.

The residual solution from stage two is directed to an evaporator where 80% of the DMF is recovered along with 100% of the unreacted IBr . The vapours are then condensed in a two stage condenser. The DMF is recovered first and then the IBr . The IBr is subsequently recycled along with the DMF. A purge system is also present on the second condenser to prevent an accumulation of the hydrobromic acid in the system. HBr is the major process contaminant and source of corrosion.

The concentrated zinc bromide solution from the evaporator is fed to another reactor to which 75% phosphoric acid is added. Reaction with the acid, under heat, produces hydrogen bromide gas and an insoluble zinc phosphate salt. Sulphuric acid was to be used in this step but was found to be too strong an oxidiser, it would have produced bromide gas instead of the desired hydrogen bromide. The dimethylformamide is unaffected by the phosphoric acid but will be miscible. The residual solution from this reactor consists of the remaining DMF, some hydrogen bromide, still in solution, and the insoluble zinc phosphate salt. The residual solution from this reactor consists of the remaining DMF, some hydrogen bromide, still in solution, and the insoluble zinc phosphate salt. This residual solution is passed through a settler to recover the solid zinc phosphate for which there is a lucrative market. The zinc phosphate is subsequently filtered to reclaim any remaining solvent. The overflow from the settler contains HBr , dissolved in DMF, which is separated in a low pressure flash drum. A 50% sodium hydroxide solution is also added. The $NaOH$ will react with the hydrogen bromide to yield a 60% sodium bromide solution.

In summary, the electrochemical process for direct conversion of halon 1301 to CF_3I encompasses production of a high value chemical in a non-oxidative environment. Its drawbacks include specificity of handling only halon 1301, very complex electrochemical reactor, cost and availability of IBr and cost and recycle of DMF.

CONCLUSIONS

The analysis presented in this paper leads to the following points:

- In our view, the existing alternative fire suppression technologies justify the immediate banning the use of halons followed by the decommissioning of halons from the existing installations.
- In our view, processes to convert halons to other chemicals exist and can be operated profitably.
- In our view, halon conversion processes provide important environmental benefits in comparison with halon destruction processes.
- Halon are potentially valuable feedstocks and should be utilised as such.

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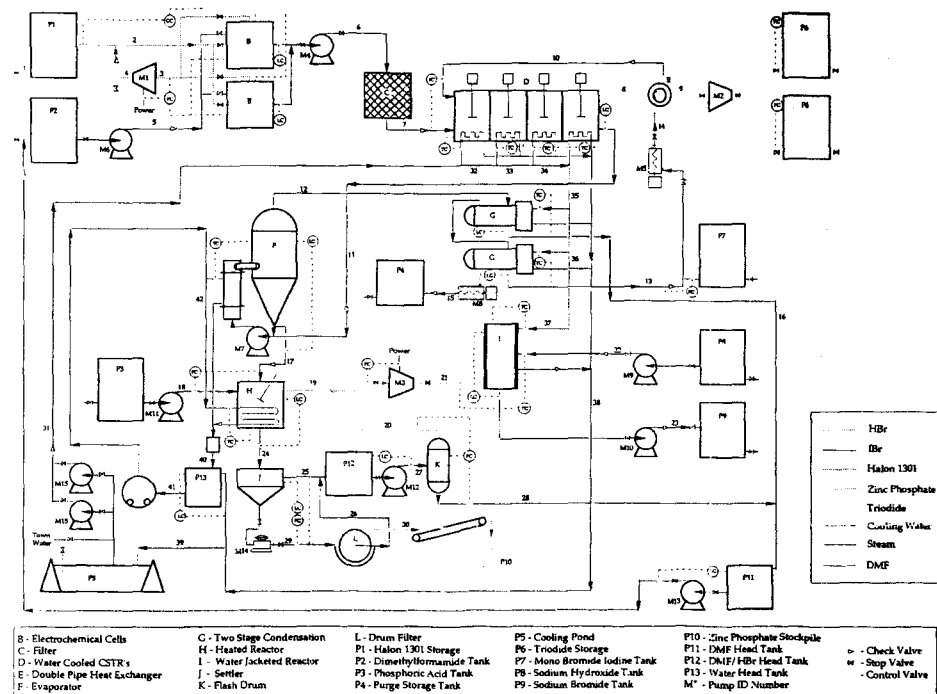


Figure 4. Flowsheet of a direct method for conversion of CF_3Br to CF_3I developed at the University of Newcastle on the basis of US Patent 4,922,041 (Naumann et al, 1990).

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