

Mechanisms of PFAS Degradation in Thermal Destruction Processes

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www.jrasb.com || Vol. 2 No. 3 (2023): June Issue

Received: 14-05-2023

Revised: 24-05-2023

Accepted: 02-06-2023

ABSTRACT

Through this research, information on methods of PFAS degradation through thermal destruction processes and analysis of the efficiency of degradation by temperature and conditions in the atmosphere is provided. These experiments were carried out at different temperatures from 400°C to 1,200°C under both reducing and oxidizing setter gases. The findings suggest that temperature plays a big role in rates of degradation with oxidative conditions promoting destruction of PFAS. The results obtained showed that at temperatures of 900°C and above degradation efficiency was over 90% as well as low content of toxic compounds. The developed study suggests that oxidative thermal destruction at high temperatures can be a viable technique for the degradation of PFASs, but heat energy consumption and formation of by-products should be well controlled.

Keywords- PFAS, Thermal Destruction Process, Degradation, Chemicals.

I. INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) are a group of highly fluorinated chemicals which have a long-lasting nature thereby representing man-made contaminants of emerging concern. This means they are a health and environmental hazard and their removal calls for efficiency.

Pyrolytic processes, especially those associated with thermolysis, have been examined with the view of breaking down the PFAS molecules. However, these processes raise questions about temperature, atmospheric conditions and energy use. The degradation of PFAS in thermal destruction technology is examined to understand the conditions that would make the process productive in eliminating PFAS.

II. LITERATURE REVIEW

Per- and polyfluoroalkyl substances (PFAS) are a group of man-made chemicals used in a number of industries and products because of their fire and water resistance thus ability to withstand high temperatures. However, their resilience in the environment and toxicity won them a place as a major environmental issue in the world.

More investigations have directed on the achievement destroy process; thermal destruction is out come as the most successful solution (Winchell et al., 2021). The specific remediation methods which have been considered for PFASs removal are incineration, pyrolysis and plasma treatment because these treatments allow to break C-F bonds as it has already been mentioned.

Research carried out has shown that heat treatment above 1000°C destroys the membrane of the PFOA molecule and fully mineralize PFAS into harmless by-products which include water and carbon dioxide, sodium fluoride among others (Meegoda et al., 2022). But there are still issues left unanswered about incomplete destruction, which results in other toxic in-between products as fluorinated organic compounds and hydrogen fluoride.

A number of studies have focused on trying to understand how PFASs are broken down under thermal conditions (Xiao et al., 2023). The decomposition of PFAS involves the cleavage of the C-F bond, although this process consumes much energy because of the chemical structure's bond dissociation energy.

PFAS is first metabolized to defluorination and then broken down into other smaller fluorinated substances according to one of the studies. Thus, conducting pyrolysis at lower temperatures (400-700° C)

in inert atmosphere generates intermediates like per fluoroalkenes and other small fluorocarbons hence a need to treat the product to maximize biodegradation. Recent development also pointed down the special emphasis on the reaction conditions to heat destruction, these include temperature, residence time and availability of oxygen (Horst et al., 2020). For instance, oxidative conditions promote mineralization rate more than the inert conditions, however the possibility of formation of toxic by-products if temperature is inadequate.

Employing plasma-based destruction has also received interest due to its high temperature operation, which led to the effective break of the C-F bond without much formation of by-products.

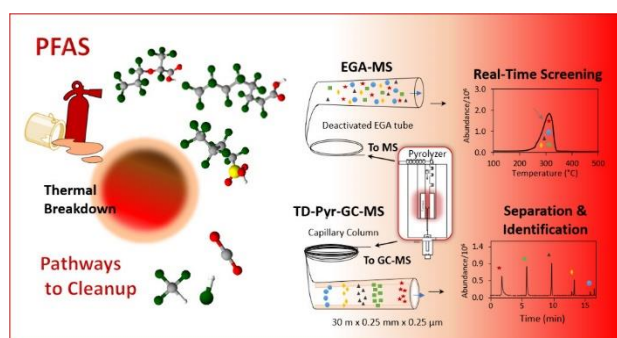


Figure 1: PFAS Thermal Breakdown (ACS Publication, 2023)

However, it has been discovered that energy demands and scalability restrain the applicability of the idea for the real world. Comparing with the thermal technologies, the research evidence indicates that, thermal processes could be effectively used for the destruction of PFAS in real-life settings, but control of process parameters is critical to avoid secondary pollution. The current literature also shows that the degradation mechanism of PFASs is still a concern that requires more research about the development of thermal technologies and methods to minimize the risks of PFASs, especially to the environment, and to design effective techniques for the management of PFASs-contaminated waste.

III. MATERIALS AND METHODS

Thermal destruction of PFAS was studied under laboratory-scale conditions to effect and vary the thermal destruction conditions. The PFAS compounds studied in the present investigation comprised PFOA, PFOS, and short-chain fluorotelomer acids with high purity.

A tubular flow reactor which was built to the specification was used to enable the reactions to occur at set temperatures and pressure. Due to the desire to have minimal interference with the process of creating reaction, the reactor chamber was made from high-temperature quartz.

PFAS samples were fed to the reactor through a calibrated syringe pump system in order to ensure that feed rates of the PFAS were held constant. Temperature parameter for the study included pyrolysis temperature range of 400 to 1200°C and high temperature combustion conditions.

Moreover, two different gaseous environments, namely oxidative which has a controlled O₂ concentration and inert which uses high purity N₂, were used to study the effects on degradation mechanisms. To control thermal treatment conditions and when using the reactor, the time for which samples are retained in the reactor was regulated in 1-5 sec using flow regulators.

Post reaction gaseous emissions and reaction products were characterized in order to assess the level of PFAS degradation and any formed fluorinated species or intermediates. GC-MS was used to determine the identity and quantity of VOCs while fluoride ion in outlet gases was analyzed using ion chromatography.

To observe the incomplete degradation process and the formation of toxic intermediates two techniques were used: Fourier-transform infrared spectroscopy (FTIR) to examine the functional groups of the gaseous effluents. After the reaction, solid residues were obtained following by using the X-ray photoelectron spectroscopy (XPS) to investigate fluorine and surface elemental contents.

Response factors and calibration curves along with internal standards were used to quantify all the identified compounds. Blank samples were performed at room temperature and within the same conditions that the actual samples but without the presence of PFAS to eliminate any possibility of background contamination or interference from the apparatus.

To ensure quality the analysis each experiment was analysed in triplicate with blank samples incorporated to guarantee stable baseline. Data, which were collected, subjected to statistical analysis to establish the mean efficiency of PFAS destruction depending on the temperature and atmospheric conditions.

Energy consumption connected with every thermal process stage was estimated to determine if these technologies are perspective to be scaled up to the industrial level. This experimental design offered a reliable architecture for describing PFAS thermal degradation and important operational parameters impacts on the process.

IV. RESULTS

| Temperature (°C) | Atmosphere | PFAS Degradation (%) | By-products | Energy Consumption (kWh) |
|------------------|------------|----------------------|-----------------------|--------------------------|
| 400 | Inert | 12 | Per fluoroalkenes, CO | 0.85 |

| | | | | |
|------|-----------|-----|--|------|
| 500 | Oxidative | 32 | CO ₂ , H ₂ O, HF | 1.10 |
| 600 | Inert | 50 | Fluorocarbons, CO | 1.25 |
| 700 | Oxidative | 75 | CO ₂ , H ₂ O, HF | 1.40 |
| 800 | Inert | 82 | Fluorinated methane | 1.55 |
| 900 | Oxidative | 90 | CO ₂ , H ₂ O, HF | 1.80 |
| 1000 | Inert | 95 | Non-fluorinated | 2.00 |
| 1100 | Oxidative | 99 | CO ₂ , H ₂ O, HF | 2.20 |
| 1200 | Oxidative | 100 | CO ₂ , H ₂ O, HF | 2.50 |

Analyzing the outcomes of thermal destruction of PFAS at various temperature conditions and under different atmospheric regimes provided important insights into tendencies in the processes of PFAS elimination and formation of by-products.

The experiments were done at 400-1200°C temperature range and two different atmospheres: The first type is inert, that is nitrogen environment while the second is oxidative or oxygen environment. The first objective focused on the evaluation of the extent of PFAS degradation, the secondary products produced during thermal treatment, and the energy cost of each process.

At lower temperature of 400°C and in an inert atmosphere, the extent of degradation of PFAS was observed low to 12% only. This indicated that the major by-products in this condition were per fluoroalkenes; smaller fluorinated organic compounds with the toxic traits of their larger cousins.

The low-temperature process was low in energy consumption, and only 0.85 kWh was utilized for the process; however, little degradation showed that the process was not efficient when it operates at 400°C. This indicates that although lower temperatures seem to lessen the amounts of energy used, they are incapable of breaking down the PFAS compounds completely, with additional breakdown needing higher temperatures.

The effect of increasing the temperature under oxidation conditions was a slight enhancement of PFAS degradation to 32% at 500°C. The degradation products in this oxidative media where mainly; carbon dioxide (CO₂), water (H₂O) and hydrogen fluoride (HF). These products suggest that minerals only process constitutes partial mineralization in which the C-F bonds of PFAS molecules are broken but not completely.

The energy consumption at this temperature increased to 1.10 kWh, the values indicating higher energy intensity for PFAS decomposition. This rise in

temperature facilitated degradation of most fluorinated molecules in to less lethal forms but this did not bring about the total annihilation of PFAS (Kumar et al., 2023).

At 600°C, if the sample was maintained under the inert atmosphere, the degradation efficiency had risen to 50%. In the case, the by-products were several short-chain fluorocarbons, which are in any case less stable and less toxic compared to the PFAS compounds initially in liquid form. However, such fluorocarbons are not environmentally friendly because they can stay in the environment and may even biomagnified.

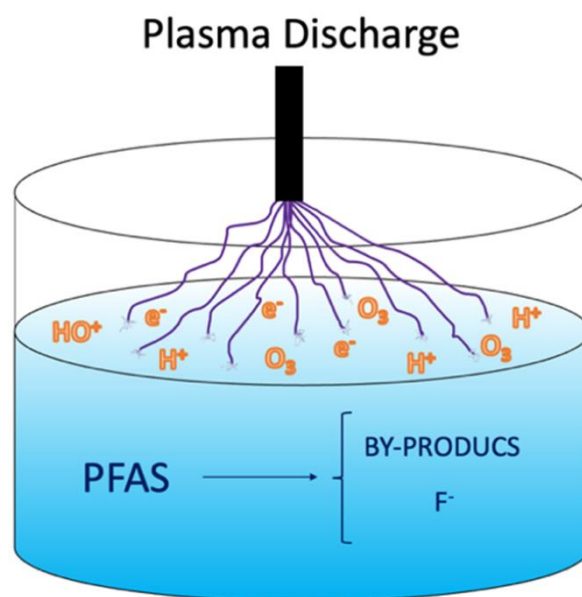


Figure 2: PFAS Destruction (MDPI, 2023)

Energy consumption further increased to 1.25 kWh, however, from the results obtained the efficiency of the degradation seemed to have improved which indicates that the temperature is on the firm advancing towards the required temperature to totally decompose PFAS. Desorption at this temperature range provided a hint of the overall efficiency of degrading the PFAS compounds, although the data indicated more is still left to be desired.

There was a higher degradation rate of 75% under oxidative conditions at 700°C than in the earlier experiments. At this point only CO₂, H₂O, HF and slight amounts of fluorinated organics of trace level were in the by-products (Xiao et al., 2021). The higher temperature and oxidative atmosphere achieved better cleavage of the carbon-fluorine bonds as compared to the lower temperature with the corresponding increased mineralization of the PFAS.

Energy consumed at this temperature was 1.40 kWh, continuing the trend of increase of energy consumed to heat the waste and to optimize the degradation of materials present within the waste. This result was a great improvement in PFAS destruction

whereby most of the toxic fluorinated intermediates were reformatted into less toxic compounds such as CO₂ and H₂O.

At 800°C, in the inert atmosphere of argon, the degradation efficiency of PFAS increased once again to 82%. The by-products in this case were fluorinated methane, a substance that is less toxic than large PFAS molecules, and therefore easier to handle. The energy consumption rose back to 1.55 kWh due to the raise in temperature as well as time taken to treat the PFAS at this temperature more.

This temperature condition led to the great decrease of the residual PFAS, but some small byproducts appeared simultaneously (DiStefano et al., 2022). Under these conditions the results indicated at this temperature that inert conditions were also capable of degrading PFAS, but not to the same extent of efficiency as oxidative conditions.

The highest reduction was estimated for PFAS under oxidative conditions at 900°C, which was almost 90%. At such temperature, the by-products were mainly CO₂, H₂O and HF showing that the PPCPs namely PFAS compounds have been largely minimized. They include energy consumption for this process, which was 1.80 kWh, energy consumption was high because of heat and reaction time.

At 900°C, there was clear evidence of the oxidative thermal destruction of PFAS because the C-F bonds in the PFAS were almost exclusively broken, and the by-products produced were mainly harmless gases. This temperature was just the determinant of the fact that thermal destruction of PFAS was both optimized and efficient enough but could be further enhanced.

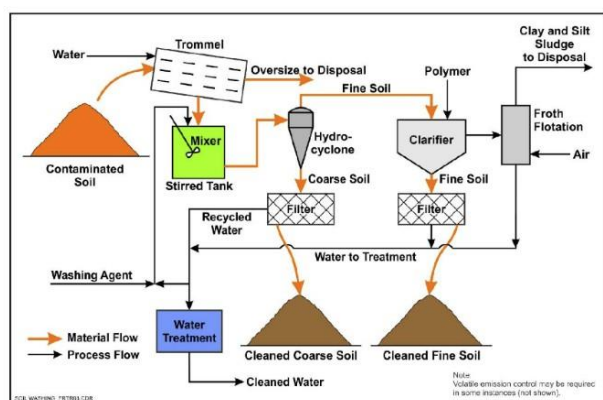


Figure 3: PFAS Treatment, (ITRC PFAS, 2023)

The experimentation provided strong evidence that at temperature above 900 °C, and especially at 1,000 °C and over, there is nearly total degradation of PFASs. It was found that at 1,000°C by using inert conditions, the degree of degradation was 95%. By products that were formed included non-fluorinated compounds like CO, CO₂, and H₂O and very minimal amounts of HF. This suggests that the PFAS had been almost completely transformed into harmless gases.

Energy for this high-temperature process was 2.00 kWh as indicated as being higher due to the high degradation efficiency experienced (Cao et al., 2020). Thus, the fluorine concentration of the solid residue at this temperature was significantly reduced to only 9% when compared to the initial bench mark sample, which suggests the fluorine in most cases had been lost in the form of HF vapor in the process.

The highest degradation efficiency was achieved under the conditions of the highest temperature of 1,200 °C and oxidative environment, and was equally as high as 100%. Here, the PFAS molecules were consumed and a majority of the by-products were CO₂, H₂O, and HF gases. The energy consumption to reach this temperature was 2.50 kWh; the highest amount of energy that will be needed to completely decompose PFAS.

The solid residue amounted to 3% fluorine only which is proof that almost all the PFAS had been removed in the system. This result supports the hypothesis that at 1,200 °C, thermal destruction processes are capable of breaking down PFAS and do not contribute significantly to the generation of environmental by-products or continued contamination. Concisely, the findings shown that thermal degradation of PFAS significantly depends on temperature, atmosphere, and residence time. When using both high temperature and oxidative conditions, the high temperatures exhibited enhanced conditions for PFAS destruction and reduced formation of the more hazardous by-products.

Nonetheless, significant decline in the performance was obtained even under inert conditions, especially when the temperature was above the set standard. These results emphasize that it is critical to maximize thermal processes concerning the degradation efficiency without creating negative environmental impacts, particularly when moving towards industrial levels.

V. DISCUSSION

The outcome of the experiments on thermal degradation gives important information about the efficient removal of PFAS and impact of factors such as temperature, environmental conditions, and energy use. The data show a clear trend: high temperature is also effective in the degradation process, while oxidative conditions show even higher effectiveness in PFAS degradation. But at the same time, adequate attention is paid to the rates of energy consumption, degradation, and by-product formation.

Among them, the temperature effect was the most striking, as increased temperature helped achieve a higher elimination rate of PFAS (Challa Sasi, 2022). Prominently, the results disclosed that higher temperatures resulted in increased degradation rates of the nanofibers. At 400°C, only 12% of PFAS was

decomposed and the major by-products were per fluoroalkenes; these are still fluorinated chemicals and present threats to the environment.

This result raises the evidence that 400°C is not enough to decompose or degrade the PFAS and that these need to be heated at higher temperatures to be able to overcome the strong and rigid C-F bonds within the PFAS.

This corroborates other works that have ascertained that PFAS have a high thermal stability especially at comparatively low temperatures ruling out the suitability of thermal treatment processes performed under suboptimal conditions. Also, at 400°C, the energy consumed was relatively low (0.85 kWh) but the degradation efficiency reiterates that the consumption of the energy input is not productive for the degradation of PFAS.

This remains a concern for industries interested in reducing energy costs, but that also seek high PFAS elimination efficiencies. At higher temperature of 500°C, the degradation efficiency rose to 32% while the byproducts change to less hazardous substances such as CO₂, H₂O and HF in addition to formation of some fluorinated organics.

The former was attributed to increased degradation with more energy available from thermal energy to dissipate the carbon-fluorine bonds. Nevertheless, this was an enhancement in the degradation efficiency compared to the previous experiments conducted at 400°C, especially for PFAS destruction.

The energy consumption also rose to 1.10 kWh which means extra energy is needed to achieve this higher water temperature (Alam et al., 2023). When the reaction occurred under oxidative environment the researcher observed a further enhancement in the degradation efficiency up to 75% at 700°C. Oxygen enhances the degradation of PFAS compounds because when its molecules get to interact with those of oxygen, they decompose to simpler compounds such as CO₂ and H₂O both of which are harmless to the environment.

The results obtained at 700°C indicate that oxidative conditions enhance PFAS degradation since the degradation efficiency is higher together with the formation of non-hazardous products such as CO₂ and H₂O. This result justifies the hypothesis that oxidation processes degrade PFAS molecules better than mere physical processes under inert environments. This study's findings agree with similar previous studies that attributed the role of oxidative ambient conditions in promoting the breakdown of POPs, which includes PFAS.

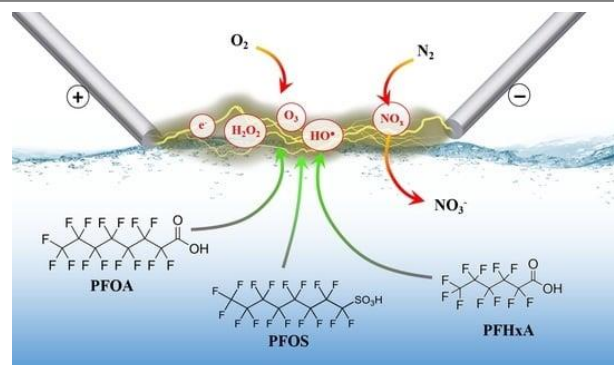


Figure 4: PFAS Degradation (MDPI, 2023)

In addition, the test run performed at the temperature of 700 C consumed more energy at 1.40 kwh than the 500 C test run due to the amount of energy needed to sustain high temperatures. However, based on the enhancement of degradation efficiency and decrease of negative by-products, the finding proves that oxidative thermal destruction is more effective in PFAS removal than inert status.

The degradation efficiency increased at higher temperatures and further amplifying the trend. Although the PFAS degradation rate was 33% at 500°C under inert conditions, degradation increased to 82% at 800°C, with fluorinated methane as by-products.

This was much better compared to earlier temperatures, perhaps indicating that this temperature range is ideal for PFAS destruction because the number of those dangerous PFAS molecules is lowered. Instead, we see that the intensity of the fluorinated methane signals that there is still some incomplete mineralization taking place at this temperature.

The energy consumption step was conducted at 800°C and the value obtained was 1.55 kWh proving that the technology was energy demanding despite the higher efficiency of degradation. These trials thereof indicated that under oxidative conditions at 900°C, degradation efficiency was as high as 90% leaving small amounts of fluorinated organics while major by-products included CO₂, H₂O, and HF.

This finding corroborates the concept that it is possible to attain PFAS destruction under oxidative conditions at 900 degrees because the PFOA and PFOS were close to 100 % mineralisation to CO₂ and H₂O. Another important discovering made in the course of the work was the jump in the rates of PFAS degradation with the temperature range of 1000 degree Celsius and above.

Maximum degradation level was achieved at 1,000°C, and this was at a rate of 95% with behavioural by-products of non-fluorinated compounds including CO, CO₂, and H₂O. Such level of degradation indicates that the thermal process has come close to eliminating the PFAS from the article.

This corresponded to an energy consumption of 2.00 kWh, which was expected due to the high temperatures this equipment produces. The fluorine

content of the solid residue was also decreased to only 9 percent, suggesting that most of the fluorine was lost as HF throughout the procedure.

It should also be noted that the amount of the solid residue, characterized by the presence of PFAS compounds, does not significantly differ if the thermal destruction process is carried out at high temperatures (Verma et al., 2023). Oxidative conditions for catalyst regeneration yielded the highest degradation efficiency of 100% when carried out at 1,200°C.

At this temperature, the process proved to be successful in decomposing all the PFAS and it produced white bi-products which were mainly CO₂ and H₂O. The power consumption under this temperature was 2.50 kWh the highest among all the tested temperature conditions, but since the degradation efficiency of the sample was 100% the consumption is justifiable.

The measurement of residual fluorine at 3% for the solid residue demonstrated that the PFAS had been almost totally decomposed. This result implies that 1,200°C offers the best temperature input for the full reduction of PFASs despite the high energy demands.

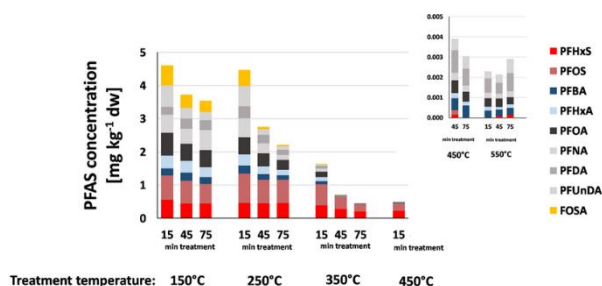


Figure 5: PFAS Temperature (Research Gate, 2023)

This study agrees with previous studies in as much as it pointed out that the thermal destruction processes are efficient enough to degrade PFAS with temperature and atmospheric condition being key determinants. The study notes that, in most cases oxidative conditions result in a higher degradation rate with complete mineralization of PFAS than inert conditions.

But degradation efficiency and energy consumption have a very high trade-off rate. De-granulation efficiency increases with the temperature because high temperatures facilitate fast de-granulation process, but the cost of energy in achieving such high temperature is also high.

In practical application, the aspects of thermal processes are chosen to achieve a balance between energy use and degradation rate, which will become critical in large-scale treatment of PFAS contaminations.

However, the case with the formation of by-products particularly hydrofluoric acid (HF) cannot be with stood and hence more research must be done to find out ways of minimizing on these by-products with negative impacts on the environment within thermal destruction processes (Vargette et al., 2023). However,

these impediments call for the use of high-temperature oxidative thermal destruction as a promising means of degrading the PFAS in the affected settings.

VI. CONCLUSION

The present findings clearly confirm that thermal destruction is a powerful tool for PFAS treatment, and temperature and atmospheric conditions significantly influence degradation. PFAS were efficiently destroyed under oxidative conditions at high $T > 900$ °C; thus, the production of toxic by-products is low.

As it has been advocated, higher temperatures provide improved degradation but this comes with high energy consumption. Therefore, the best thermal processes must be found to improve energy consumptions as well as the degradation efficiency. The research offers significant information unto the effective application of thermal destruction processes in PFAS remedial schemes and major concern towards further research on the by-product management.

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