



Application of Aries Process Technology to the Problem of PFAS Contamination

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ABSTRACT

In the treatment of industrial and domestic waste water sludge, perfluoroalkyl and polyfluoroalkyl substances, collectively known as PFAS, have become a serious issue due to their very stable chemistry, their tendency to bioaccumulate, and their harm to human health. A review of the available literature indicates that the Aries fluid bed gasifiers offer an effective new solution to treat and destroy PFAS in domestic waste water sludge. Other potential feedstocks with PFAS contamination can also be processed in either gasifier. Pilot scale testing at low temperature shows that PFAS will be volatilized from the sludge at very high percentages. The operating temperature of 1250 °F and the residence time in the fluid bed gasifier, and 1600 °F in the downdraft gasifier, should give time for thermal decomposition of most PFAS compounds which mostly thermally decompose in the 660 °F – 930 °F range. The ability to decompose PFAS is enhanced by the presence of a large fraction of hydrogen in the producer gas. The pass through the thermal oxidizer at 1800 °F gives another opportunity for the most stable PFAS compounds, which can require temperatures as high as 1000°C (1830°F) to decompose completely, to be destroyed to some degree. The combination of the gasifier and the thermal oxidizer allows both reducing and oxidizing reactions to attack PFAS. Though the reaction rates are much slower, the hydrated lime added to the emissions control offers an additional opportunity to destroy PFAS.

The combination of Aries gasification technology with the thermal oxidizer and hydrated lime-based emissions control system offers a unique three step solution for the destruction of PFAS that could revolutionize the treatment of domestic waste water sludge and other PFAS contaminated solids. Through these three separate steps to destroy PFAS in the Aries gasification systems, opportunity exists to produce a fuel gas, by-products, and beneficial use products such as biochar with appreciable or complete reductions in PFAS contamination compared to the incoming biosolids.

INTRODUCTION

What is PFAS?

Perfluoroalkyl and polyfluoroalkyl substances, collectively known as PFAS, are chemicals that achieved wide use in commercial and industrial applications due to their excellent resistance to water and grease. Many of the uses took advantage of these properties to provide non-stick coatings for cookware, water resistance to clothing, and stain repelling properties to various fabrics. They have also widely been used in firefighting foam.

PFAS chemicals are alkanes, chains formed from singly bonded carbon chains with a functional unit on the end such as carboxyl (COOH), sulfonic (SO₃H), sulfonamide (SO₂NH₂), alcohol (CH₂CH₂OH), etc. Perfluoroalkyl compounds are fully fluorinated on the alkane chain. Polyfluoroalkyl compounds are not fully fluorinated with at least one atom in the chain having a bond to an atom other than fluorine, typically hydrogen or oxygen. Normally, at least two atoms in the chain will still be fully fluorinated. Polyfluoroalkyl compounds often decay into shorter perfluoroalkyl compounds. The fluorine bonds make the perfluoroalkyl more stable both because of the strength of the carbon-fluorine bond and because of the shielding from attack of the carbon-carbon bond by the fluorine atoms.



Properties of PFAS

PFAS compounds can be found in either acid form or as the anionic form such as when dissolved in water or in salt form. The acid and anionic forms have different properties and the acid forms are more thermally stable. Most PFAS compounds in the environment are found in their anionic form. Different cations in the PFAS salts also affect the stability of the anion. Another factor influencing the stability of PFAS is the length of the chain. The wide variety of carbon chain lengths, degree of fluorinated bonds, acid or anionic forms, and varieties in possible functional groups on the head end of the chains means that there are hundreds of identified PFAS with a variety of chemical and physical properties.

The stability of the perfluorinated chains in particular lead to them often being referred to as “terminal” degradation products. They are extremely stable and are considered to be non-degradable in the environment.

They are also often referred to as “forever chemicals” because of their long life in the environment. This stability and widespread use have led to PFAS being found at low concentrations in many locations in the environment. PFAS can cause human health effects such as reproductive and developmental effects including reduced fertility, liver and kidney damage, immunological effects, cancer risks, and harm to growth, learning, and behavior of infants and children. PFAS also will bioaccumulate.

PFAS TREATMENT AND CONTROL

Thermal decomposition is a relatively straightforward method to treat materials such as soil that is contaminated with PFAS. The method is typically effective for a wide variety of PFAS compounds. Decomposition temperatures for PFAS are typically in the 350 – 500 °C (660 – 930 °F) range, though for particularly stable acid forms, treatment at temperatures in excess of 1000 °C (1830 °F) may be required for complete decomposition.

Many of the other emerging PFAS control and contamination remedial technologies center around removing the substances from contaminated water and are well documented. The topic of beneficial use products such as biosolids for fertilizer from the waste water treatment processes is a new challenge to addressing the emerging risks of PFAS.

BENEFITS OF THE ARIES GASIFICATION TECHNOLOGY PROCESS

Process Description

Aries has two separate patented gasification technologies that have applications in the reduction of PFAS. For waste water sludge, the primary technology would be the Aries fluid bed gasifier. This is an atmospheric, bubbling bed, air blown gasifier sized to gasify nominally 100 tons/day of dried sludge or other suitable fuels. For waste water sludge, the gasifier operates at approximately 1250 °F in the fluid bed section of the gasifier.

The second gasifier technology is the third generation of the Aries large format downdraft gasifier. This is the world’s largest downdraft gasifier and is sized to gasify nominally 65 tons/day. The downdraft gasifier is suited for larger feed material, such as chipped wood waste, and lower ash material. For sludge applications, the downdraft gasifier can process up to 10% sludge mixed with other fuel.

The Aries process provides three distinct steps that function in tandem to destroy PFAS.



Figure 1 shows an example of the typical process flow diagram for an Aries fluidized bed sludge processing gasification plant. After the feed material is received and processed as needed, the dried biosolids fuel is fed to the Aries patented gasifier. The gasification process is the first step and the primary means to decompose PFAS through thermal decomposition enhanced by hydrocracking reactions from the hydrogen present in the producer gas.

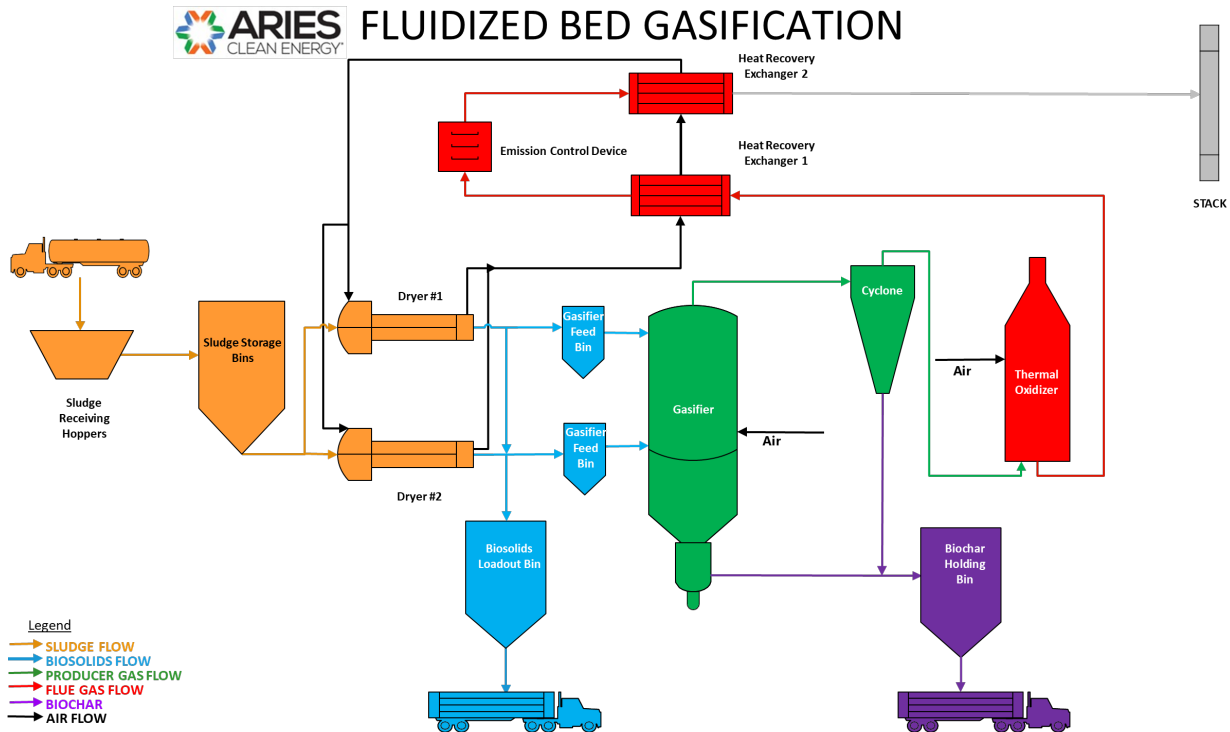


Figure 1. Typical Aries Fluidized Bed Gasification Process

In a typical installation, the producer gas is combusted in a thermal oxidizer to provide heat to the system. In the case of a sludge treatment facility, as shown in Figure 1, the heat is used to dry the incoming sludge. In other applications, the heat is used to generate electricity or to provide heat to other processes. The thermal oxidizer provides a second step for the Aries process to destroy PFAS. The thermal oxidizer operates at 1800 °F or higher in order to oxidize the carbon monoxide in the producer gas to be within the air permit emissions regulations limits. This higher temperature is also a key feature of the second step in the Aries process that enhances the decomposition of the most stable PFAS. The thermal oxidizer adds an oxidizing environment which complements the reducing environment inside the gasifier and creates multiple paths to PFAS decomposition.

The flue gas from the thermal oxidizer goes through heat recovery equipment and an emissions control system that operates at around 700 °F before being discharged through the stack. The third step in the process that serves as a final safeguard to enhance destruction of PFAS to harmless gas molecules is the injection of sorbent in the emissions control system. Sorbent treatment enables PFAS decomposition through hydrodefluorination reactions enhanced by the presence of calcium hydroxide.



Both gasifiers produce a biochar that can be used for land application for soil enhancement. After treatment in either gasifier, however, the biochar will not present the typical problems, including PFAS contamination, that plague the current use of biosolids for land application.

Gasifier

The primary method of destruction of PFAS in the gasifier is by thermal decomposition enhanced by the presence of hydrogen in the producer gas which increases the reaction kinetics of the decomposition through hydrogen cracking of the carbon bonds. Hydrogen fluoride, released during the thermal decomposition, can also attack the PFAS bonds. The gasifier provides a relatively long residence time at the elevated temperatures. The sand bed is maintained at about 1250 °F during sludge gasification in the fluidized bed gasifier. Residence time in this bed should be 2 – 3 seconds. There should be another 6 – 8 seconds of residence time in the freeboard where the temperature will slowly decrease from 1250 °F to about 1150 °F. In total, the PFAS should have about 10 seconds of residence time in the gasifier before exiting in the overhead line to the thermal oxidizer.

Because of the many different forms of PFAS, it is expected that the gasifier will be effective at thermally cracking most, but not all, PFAS chemicals. The most difficult compounds to thermally decompose are the perfluoro compounds because the fully fluorinated compounds present the strongest bonds to crack.

Studies of perfluorooctanesulfonic acid [PFOS] have shown that it decomposes into a perfluoro aldehyde at 1000 K (1340 °F) with a half-life of 0.2 sec. The resulting aldehyde, which transforms into a perfluoro carboxylic acid, has been shown in other studies to rapidly decompose with a half-life of 0.2 sec at only 350 C (660 F).

Kissa (2001) presented data for perfluoro chains of various lengths and with different cations in the salt. The data indicated that the decomposition temperatures of salts of perfluoroalkanesulfonic acids decomposed in a temperature range from 215 to 371 C and that salts of perfluoroalkane sulfonates decomposed in a range of 386 °C to 532 °C. This compares very favorably to the 675 °C operating temperature in the fluid bed gasifier and 870 °C in the downdraft gasifier.

Another study looked at the decomposition of ammonium perfluorooctanoate in the range of 196 °C – 234 °C. From this kinetic data, the decomposition rates at higher temperatures was extrapolated. At 350 °C (660 °F), the half-life was less than 0.2 sec.

Many of these studies of the thermal decomposition of PFAS are conducted either in the context of incineration where oxygen is present or in the context of pyrolysis in a nitrogen atmosphere. In a practical situation, such as in the gasifier, the presence of hydrogen will lower the effective decomposition temperature through hydrocracking of the alkane chain. One reference, ITRC, states that “the mineralization temperature may be lower due to the presence of other substances that contain hydrogen.”

Thermal Oxidizer

The above references to the decomposition temperatures for the gasifier also apply to the thermal oxidizer. The decomposition kinetics increase rapidly in rate with increases in temperature. The thermal oxidizer for the gasification system is already specified to have a gas residence time of at least 1 sec at a temperature of at least 1800 °F in order to completely oxidize the carbon monoxide present in the producer gas. This high temperature gives a second step where the more difficult compounds to fully



decompose are passed through an incineration zone at significantly increased temperatures in an oxidizing environment.

Emissions Control

The final step to decompose PFAS takes place in the emissions control system. One study looked at the effect of calcium compounds on the decomposition of PFAS. Of three compounds tested, the most effective was calcium hydroxide which is the sorbent used in the emissions control system for sulfur and halogen control (as hydrated lime). Testing showed significant decomposition of PFAS at temperatures exceeding 400 °C (750 °F) through hydrodefluorination reactions. This is within the range of temperatures at which the emissions control system can be operated. It should be noted that these tests were carried out with the PFAS in contact with the calcium compounds for several minutes. The slow kinetics of the reaction between calcium compounds and PFAS would not lead to this being considered a primary control method but might offer an opportunity for minor polishing of any compounds that survive the gasifier and the thermal oxidizer.

ARIES PFAS DESTRUCTION TESTING

In October 2019, Aries contracted with the Energy & Environmental Research Center (EERC) at the University of North Dakota to conduct testing of automotive shredder residue (ASR) in a pilot scale bubbling fluidized bed gasifier at the relatively low temperature of 950°F. The feed material and the char were both collected and analyzed for PFAS. Gas analysis was not performed. . No residual PFAS was detected in the bed material nor in the elutriated char material collected from the producer gas stream by the cyclone. Residual PFAS was detected in the char collected in the filter downstream of the cyclone. Based on the estimated cyclone efficiency and feed composition, the residual amount of PFAS in the filter char equates to about 99.5% removal. Figure 2 shows the measured levels of PFAS in the solids samples taken during the testing. One item to note about the configuration of the test units is that the filter vessel is between the cyclone and the thermal oxidizer. In the Aries process, the filter is an integral part of the emissions control system for the flue gas and therefore the material collected on the filter would instead pass through the thermal oxidizer.

Sample Location	PFAS Concentration (ppb)
ASR Feed	9.121
Bed	0
Cyclone / Bed	0
Filter	1.507

Figure 2. Measured PFAS concentrations in pilot testing with ASR

Because of the lack of gas analysis in this initial testing, it remains possible that some of the PFAS was volatilized but not decomposed, though it is very unlikely that any PFAS would survive the high operating temperatures of a thermal oxidizer. These initial positive results at very low temperatures are however very promising and further testing and gas analysis will be needed to confirm the decomposition of PFAS.

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