

DEECOM®: A SUSTAINABLE PROCESS USED IN VARIOUS RECLAMATION PROCESSES

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Abstract

The manufacturing of various polymers utilizes complex metal parts which are reclaimed for repeat use. Traditional reclamation methods utilize solvents and other chemicals which have a high energy demand and involve expensive disposal methods – some of which involve landfills. In response, the DEECOM® technology, a solvent-free and relatively low temperature reclamation technology, is based on a pressure swing technique designed to physically disrupt and remove polymer from parts. The mechanism of the new process results in filter reclamation procedures that are relatively friendly environmentally, have a higher degree of sustainability, and generate a smaller carbon footprint compared to traditional methods.

In addition to polymer filters, the DEECOM® technology has more recently been utilized in other reclamation applications. These include the reclamation of polyester from PET bottles, carbon fiber from epoxy based composites, as well as, the reclamation of spent activated carbon loaded with organic components.

This paper describes the development of the novel, patented, and solvent free low temperature cleaning & reclamation process known as DEECOM®.

Introduction

As part of our development program, we reviewed the major cleaning technologies. These may be summarized as high temperature solvent cleaning, pyrolysis in the presence and absence of air and high temperature hydrolysis [1]. All were preceded to a greater or lesser extent by polymer melting and followed by one or

more post treatments such as acid or alkali washing and ultrasonic cleaning.

For many years Glycols have been the high temperature solvents of choice and were considered a reliable and relatively safe depolymerization method of cleaning polymer melt filtration equipment. However in the long term, it may not be viable because of the small amount of degraded polymer and solvent waste the process produces. Pyrolysis techniques seem to offer an environmentally friendly solution [1]; but it must be remembered that the carbon in both the TEG and in the polymer is derived from ancient carbon and burning them will contribute to the net global Carbon Dioxide loading.

Furthermore pyrolysis techniques run the risk of sensitizing or damaging the delicate filter media. This is particularly true if pyrolysis in a reducing atmosphere, resulting in elemental carbon deposits, is followed by pyrolysis in air [1]. High temperature steam hydrolysis of certain polymers is well understood and, in theory, the treatment of these polymers to yield the constituent monomers, for example, Ethylene Glycol and Terephthalic acid from Polyethylene terephthalate, is attractive [1]. However, the reactant material is a polymer, whereby, it is either in the solid or liquid state and not in solution. Consequently the reaction rate, even at high temperatures will be low, as the process is a two-phase reaction; the rate being limited by the surface area of the polymer. These predictions were confirmed by experiment. Finally hydrolysis is only relevant to the range of polymers containing a hydrolysable unit [1].

Materials

Earlier crude experiments carried out in the plant had suggested that in addition to hydrolysis it should be possible to remove the polymer film by using a pressure swing technology driven by clean superheated steam. This latter process is, we believe, a physical disruption of the polymer and as such is quite different from hydrolysis, which is a chemical reaction [2]. It was decided to study, firstly hydrolysis using PET as a model polymer. A small pressure vessel was constructed that was capable of treating a few grams of polymer and was fed from a generator by a stream of clean superheated steam [3]. In each of the experiments a sample of polymer weighing 5.00 gm was used. The products of the reaction were collected as a condensate from an outlet condenser and the liquor remaining in the vessel after cooling. These two solutions were combined and their total volume measured. Initially it was decided to try to measure the amount of hydrolysis at different temperatures by measuring the Chemical Oxygen Demand (COD) of the Chemical Oxygen Demand (COD) of the condensate. These results are shown below (Table 1 and Figures 1&2).

Table 1. Degradation of PET at different temperatures using Clean Super Heated Steam.

Temperature (°C)	Condensate COD (mg/L)	Total COD (mg)	Total Degradation (%)	Total Degradation Log (%)
0	0	0	0	
200	80	17.5	0.35	-0.456
250	500	210.5	4.21	0.624
300	1070	1,355	27.1	1.769

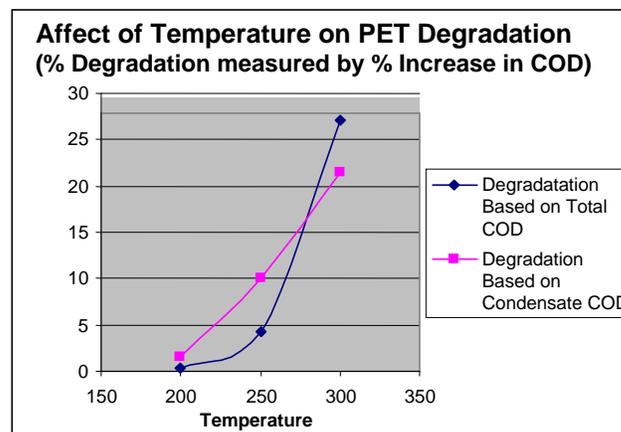


Figure 1. Affect of Temperature on PET Degradation

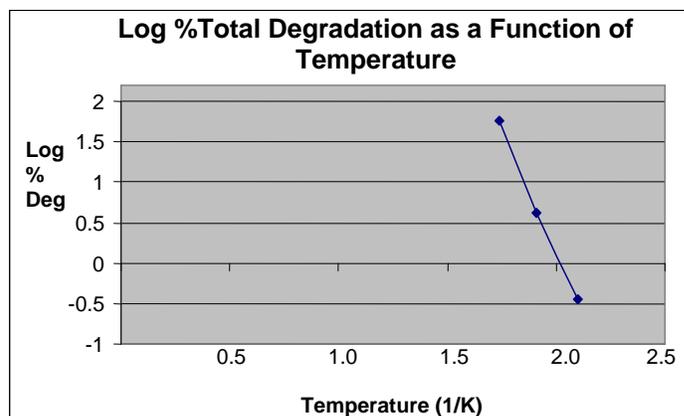


Figure 2. Degradation (hydrolysis) of PET, (Log % Total Degradation vs 1/K) illustrates Arrhenius Plot (page 3)

The hydrolysis products were analyzed qualitatively using Gas Chromatography inked to Mass Spectrometry (GC/MS). The aqueous sample was initially ethylated and then extracted into Methylene Chloride. The Methylene Chloride sample was then dried and injected into the GC/MS unit. A total of three samples from three experiments carried out at different temperatures were analyzed in this manner.

It may be concluded that at high temperatures the polymer is hydrolyzed to a mixture of products. Some is hydrolyzed completely to Teraphthalic Acid and two carbon fragments derived from ethylene glycol [1]. The majority however appears to be in a range of oligomers, possibly representing three to five or six monomer units. It is also clear (Figure 1) that

little or no hydrolysis occurs at 200°C and that only a small amount, 4 – 5 %, occurs at 250°C.

The assumption that the COD is a rough measure of the degree of hydrolysis is reasonable as the GC/MS results indicate that at higher temperatures the polymer chain is broken into smaller fragments by hydrolysis of the ester linkage [1]. However it must be remembered that in the small test rig using small samples of polymer, nearly ideal conditions are achieved and that in the cleaning of a large complex filter, conditions may be less than ideal. Despite this the results (Figure 1) suggest that a typical chemical reaction is occurring as the amount of hydrolysis increases with temperature. The COD values may be interpreted as equivalent to rate constants as the same mass of reactant and reaction time were used in each experiment. By the same argument the logarithmic plot (Figure 2) may be interpreted as an Arrhenius plot. All of which demonstrates that this is a normal chemical reaction, probably pseudo first order with the steam being the reactant in excess and the rate limiting step being the surface area of the polymer.

Finally the key observation is that little hydrolysis occurs below 250°C. In contrast it has been demonstrated, during earlier experiments, that effective and complete cleaning of contaminated filter units may be carried out at temperatures below 250°C using a pressure swing technique (the **DEECOM**® process). An example of a low temperature cleaning cycle will be presented below.

The Development Program

It was not possible to study pressure swing technology using the small unit described above; consequently an experimental pilot plant capable of treating small commercial sized filter units and single filter candles was built. The outstanding success of this device led to a decision to immediately build a commercial scale treatment plant and all further

development work was carried out using this plant.

DEECOM® uses two stages that alternate throughout a full cycle to effectively remove polymer and filler contaminants. The filter unit to be cleaned is mounted vertically in the pressure vessel. Firstly, superheated steam is fed through the vessel at low pressure this, depending on the temperature will melt or soften the polymer and at temperatures above 250°C a small amount of hydrolysis will occur. Heavily contaminated filter units are treated for sufficient time to allow the polymer to melt and flow into the base of the vessel [2].

The pressure swing cycle is then started. An outlet valve is closed and the pressure and temperature are allowed to build up to a predetermined value. The pressure in the vessel is then rapidly decreased, by opening a specially designed valve, causing what is known as ‘explosive decompression’. Whilst having no effect on the integrity of the metal parts, the steam can penetrate fissures in the polymer where it condenses as superheated water. On decompression it boils instantly cracking the polymer and carrying away broken chips along with the softened, degraded polymer fragments on the outer surfaces. The pressure swing cycle may be repeated at frequent intervals and controlled automatically. Validation tests have confirmed that repeated cleaning of filter elements using **DEECOM**® has no detrimental effect on the integrity of filter media or metal structure. It may be compared to a molecular scale hammer and chisel, removing the outer coating of contaminant each time decompression occurs [2].

Once the majority of contaminant has been removed and the superheated steam can envelope the filter media itself, on decompression, the steam is carried out of the media, taking with it any filler pigment or catalyst particles which themselves are unaffected by the processes. Generally the bulk of such inert materials are removed by the

steam. In some cases, particularly filter units that have not been well cleaned in the past, residual solids may be removed by washing or ultrasonic treatment [2].

The process is effective for all types of polyesters. The combination of molecular decomposition and mechanical shattering of polymer chains also means **DEECOM®** can be used in the removal of substances not associated with standard hydrolysis type processes. It has also been shown that it is particularly effective in treating plasticised polymers. In conclusion, it has been shown effective in successfully degrading many polymers including PET, polyamides, ABS resins and co-polymers, PVC and all plasticised polymers.

The Commercial Program

The system has been trialed on large variety of polymer filter types; discs and candles, single units and full stacks, up to 96 discs and 37 candles. All of these development projects have consistently reached successful conclusions. A number of other technologies for the cleaning of polymer filtration equipment have been outlined above. Some of these technologies use steam in some state as a cleaning medium but **DEECOM®** is unique not only in its technique but also its ability to efficiently clean a filter element of polymer and associated fillers without causing damage to filter media and yet also having the potential to extend useful filter life beyond that expected when using traditional cleaning technologies.

The aim of substituting TEG solvent processing with **DEECOM®** was achieved relatively early in the development project – it then became clear that **DEECOM®** is further capable of reducing the need for, and may even negate, supplementary cleaning operations. It is these supplementary operations; ultrasonic tanking, high pressure washing etc that add significantly

to the cost of cleaning as filter elements are often handled and treated individually. The cost saving implications of reducing supplementary operations are obvious.

Case Study 1

Rejected PET Candle Filters

Trials have shown that filter elements which have been regularly cleaned using TEG processes and have subsequently been rejected, having reached the end of their useful life, can be re-claimed by the **DEECOM®** process to a state at which they can be returned to service in a polymer line.

Case Study 2

PET Disc Stacks – Cleaned without supplementary processes.

Disc filter stacks from a large film manufacturer were trialed extensively in the early development of **DEECOM®**. These stacks were traditionally un-drained and plugged with between 5kg and 20kg of frozen PET. Trials on filter stacks of up to 96 discs repeatedly showed that benchmark validation results were attained after a single **DEECOM®** process only.

Case Study 3

Elastomer Filter

Trials have been carried out on a pilot sized filter from an elastomer plant that was found successful. After a six-hour cleaning process the bubble point and mass validation tests were passed with results equal to those of TEG cleaning. The mechanism of degradation is such that no hazardous by-products are created. Again benchmark validation results were achieved without supplementary cleaning operations.

Case Study 4

PET Plant. Reduction of initial pressure surge on return to production line

Filter stacks cleaned using the DEECOM® system have shown significantly reduced levels of surges when returned to polymer lines. Consequently, full-quality production can resume sooner than has been possible using alternative cleaning methods, i.e. higher levels of saleable polymer can be produced more quickly.

Case Study 5

A number of successful DEECOM® cleaning processes have been carried out, notably on PET disc filter stacks, at relatively low temperatures. The maximum temperatures of these experiments ranged from 234°C and 270°C. Even at these low temperatures benchmark weights were achieved in a single step, without supplementary cleaning.

Conclusions

It can be seen from the information presented above (Case Study 5.) that complete cleaning of the filter has been achieved at a temperature where little or no hydrolysis occurs (see Figure 1). Consequently when the DEECOM® process is operated at higher temperatures, some hydrolysis will occur but it will be minimal, the major cleaning action will be explosive decompression.

In the cleaning of PET filtration equipment, DEECOM® has been shown capable of surpassing the results of TEG solvent cleaning technology. The absence of high temperatures solvents drastically improves the health and safety conditions of a cleaning facility whilst also removing the cost burden of purchasing, transporting and disposing of large volumes of that solvent. A further environmental benefit is that there

are no contaminated solvent disposal problems. The additional benefit of reducing or negating subsequent washing operations means that significant cost savings can be made on cleaning of filter equipment.

In summary, the benefits of DEECOM are:

- (1) No solvent required,
- (2) Does not depend on hydrolysis,
- (3) No high temperature pyrolysis,
- (4) Mild process,
- (5) Low temperature process,
- (6) Low energy process,
- (7) Reduced levels of waste

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