COMBUSTION AND HEAT RECOVERY FROM POLYMERIC MATERIALS

by

Wallace Hart
Manager Process Engineering
John Zink Company

Introduction

All plastics manufacturing processes produce some off-specification product, and some produce by-products for which no adequate market has been developed.

Historically the off-spec material that could not be "blended off", and the by-product material that could not be sold has been disposed of by land filling. This is not only expensive but, more and more, is being prohibited by environmental authorities.

The combination of environmental problems and rising fuel costs has made combustion of these waste plastics for steam generation a very attractive proposition. The technology involved, however, is not simple, and, for some plastics, only recently has become available.

This paper presents a continuous combustion and heat recovery process applicable to most waste plastics, but designed primarily for atactic polypropylene. Emphasis is given to atactic polypropylene for two reasons--(1) it is one of the most plentiful waste plastics to be disposed of, and (2) the problems it presents fairly well cover the gamut of problems one is likely to encounter with any other plastic.

A block flow diagram of the process is shown in Figure 1. It involves a two-stage combustion system, steam generation by means of a waste heat boiler, and flue gas clean-up equipment. After a brief review of the problems that can arise, each step of the process will be discussed in detail.

The Problems

Most plastics have in common the property that they cannot readily be liquified and atomized for burning in suspension. Nor is it generally practical to shred the solid into a fine, air-veyable form for suspension burning.

The most practical method seems to be that of "hearth-burning", wherein the plastic--in any form--is introduced onto the floor of a furnace, whereupon it burns at a rate proportional to the exposed surface...
area. The problem here is controlling the combustion rate—frequently in the face of batchwise and erratic feedrates.

If the plastic contains considerable ash—as some atactic polypropylene does—the combustion process is further complicated by potential blinding of the polymer by an ash layer which seriously retards combustion rate. Depending upon the constituents of the ash, it can also be a potential refractory slagging agent, and can certainly cause fouling of the waste heat boiler. In any event it must eventually be removed from the flue gas.

Some plastics, upon combustion, produce acid components—such as HCl and P₂O₅ in the flue gas; and these can pose serious corrosion problems in the downstream components. Obviously PVC produces HCl, but perhaps not so obviously, some atactic polypropylene may produce both HCl and P₂O₅.

Fortunately, we at John Zink Company did not have to solve all these problems simultaneously. From our years of experience in the pollution control field involving combustion, gas conditioning, heat recovery, particulate removal, absorption, etc., we had developed solutions to many of these problems before we tackled atactic polypropylene.

**Primary Combustion**

The overall reactions associated with plastics combustion are illustrated below (using polypropylene as an example):

\[
\text{Solid } [\text{C}_3\text{H}_6]_n + \text{heat } \rightarrow \text{liquid } [\text{C}_3\text{H}_6]_n \quad (1)
\]

\[
\text{liquid } [\text{C}_3\text{H}_6] + \text{heat } \rightarrow \text{C}_3\text{H}_6 + \text{other gases} \quad (2)
\]

\[
\text{C}_3\text{H}_6 + \text{O}_2 + \text{CO}_2 + \text{H}_2\text{O} + \text{heat} \quad (3)
\]

\[
\text{C}_3\text{H}_6 + \left(\frac{\text{CO}_2 + \text{heat} + \text{CO} + \text{H}_2}{\text{H}_2\text{O}}\right) \quad (4)
\]

\[
\text{CO} + \text{H}_2 + \text{O}_2 + \text{CO}_2 + \text{H}_2\text{O} + \text{heat} \quad (5)
\]

Even though the plastic may be introduced as a solid the rate-limiting step seems to be the pyrolysis reaction (2) which is basically a heat transfer problem.

The rate of heat transfer to the molten plastic is proportional to the temperature, the surface area, and the turbulence. Surface area is not readily controlled—especially when the plastic is introduced as solid chunks in a batchwise manner. As one might expect, the best way to control combustion rate is to use a two-stage system. In the first stage the polymer undergoes partial combustion, pyrolysis, and reforming in a sub-stoichiometric environment. Rate is controlled by regulating the combustion air rate.
The pyrolysis gases are then burned in a second stage under excess air conditions to the complete destruction of all combustible matter. In our process a high degree of turbulence is maintained in the pyrolysis zone—not only to enhance pyrolysis rate but also to disturb any ash layer that may tend to blind the polymer surface. In fact, a key feature of our process is that such a high degree of turbulence is maintained that all the ash is entrained into the pyrolysis gases and carried out of the reactor so that mechanical ash removal methods are unnecessary. This also permits the process to be as continuous as the polymer feeding system.

This turbulent environment is achieved by proper design and placement of the primary air injection nozzles, and in some cases by recycling combustion gases from downstream of the waste heat boiler.

Theoretically, the pyrolysis section may be operated at any temperature from say 922° K (1200°F) to over 1367° K (2000°F). This is related to the amount of air admitted to the unit m² of hearth area. The higher the temperature, of course, the more plastic is consumed per m² of hearth area.

The thing that dictates the upper practical limit is the ash fusion temperature. If the ash softens and becomes tacky it tends to conglomerate and becomes nearly impossible to entrain away from the pyrolyzing plastic. (Theoretically, one could operate well above the ash fusion temperature such that the molten ash would "layer out" beneath the plastic and could be "hot tapped" into a smelt tank. This however, creates more problems than it is worth in most cases.)

It turns out that very satisfactory pyrolysis rates of 146-244 Kgs/hr-m² (30-50 lbs/hr-ft²) can be readily achieved at temperatures in the 922-1144°K (1200-1600°F) range—where it is possible to avoid ash fusion in nearly all cases.

It is worth noting that an added advantage to operating this first stage under "reducing" conditions is that with melamine type resins the formation of NO x can be minimized.

Secondary Combustion and Heat Recovery

Along with normal flue gas components the pyrolysis gases from the primary chamber may contain various hydrocarbon fragments, CO, H₂, coke, ash, HCl, and compounds of phosphorous or sulfur.

Complete oxidation of all combustibles is achieved by injecting secondary air in such a way as to achieve rapid and thorough mixing, and then providing sufficient residence time for all reactions to proceed to "equilibrium". Normally this reaction is carried out at about 25% excess air.

If no provision is made for cooling, the temperature in the oxidation chamber can be in excess of 1922° K (3000°F). To operate at such temperatures is to invite refractory problems.
Furthermore, it is desirable to exhaust the gases from the oxidation furnace directly into a waste heat boiler for steam generation.

Once again the problem of ash fusion enters the picture. One cannot operate a boiler on flue gas containing fused ash. The ash will freeze onto the tubes as a "glass" that cannot be removed by soot blowing. The "glass" will accumulate until the boiler is totally inoperable.

It is imperative, therefore, that the gases entering the boiler be at such a temperature that the ash is solidified and friable. Fortunately, in many cases this can be as high as 1367 - 1478°C (2000 - 2200°F). In a few rare cases it may be as low as 1033 - 1089°C (1400 - 1500°F).

For this reason the temperature in the oxidation furnace is controlled so as to avoid ash fusion. This may be done in many ways—such as water injection, high excess air rates, or cool gas recycle. Recycling cool gases from downstream of the boiler is by far the preferred method because this maximizes heat recovery. Figure 2 shows a comparison of thermal efficiencies using water, excess air, and recycle.

Even with solidified ash the boiler design must be quite specialized in many cases. To accommodate soot blowers the conventional approach is to use a water-tube boiler. If the ash is erosive velocities should be limited to about 15.24 - 18.29 m/sec (50 - 60 ft/sec). Fins can be used but spacing should be limited to about 80 fins/meter (24 fins/ft).

If acidic components such as HCl or P2O5 are present serious consideration must be given to metal temperatures throughout the boiler. Dew point must be avoided. While this is not too difficult to do with HCl, it can be next to impossible if there is a sufficient amount of P2O5. On the other hand metal temperatures should not be too high either. HCl can be somewhat corrosive to carbon steel at temperatures much above 589°C (1000°F).

**Flue Gas Clean-Up**

Flue gas clean-up may involve particulate removal and/or absorption. Particulate removal may be accomplished with cyclones, venturis, ESP's, bag filters, etc. A typical particle size is listed in Table I. The particles are quite coarse compared to what one finds from suspension burning processes.

As a result cyclones can be quite effective in removing the bulk of the particulate. Some types of atactic polypropylene, however, may contain up to 10% ash. At these high dust loadings it is often not possible to meet today's stringent emission requirement with cyclones alone.

In these cases, however, it may still be advisable to use a hot cyclone upstream of the waste heat boiler to reduce fouling and soot blowing requirements, then "polish-off" the particulate in a high efficiency device on the backend of the system.
If the plastic contains chlorine, a packed absorber can be provided after the waste heat boiler to absorb the HCl and produce an HCl product of up to 20% concentration for disposal or possible reuse.

**Economics**

Figure 3 presents a flow diagram of a system designed to burn 454 kg/hr (1000 lbs/hr) of atactic polypropylene containing 8-10% ash. In this particular case no acidic components are present in the flue gas.

The net heating value of the plastic is about 45,350 kJ/kg (19,500 Btu/lb), so the total heat release in the system is about $19.8 \times 10^6$ KJ/hr ($17.9 \times 10^6$ Btu/hr). The system generates 7,170 kgs/hr (5,800 lbs/hr) of saturated 4,238 KPa (600 psig) steam from 378°C (220°F) boiler feedwater. This represents a thermal efficiency of almost 90%.

The economics of the system should be about as follows:

A. Major Equipment Cost  
   (Includes all vessels, shop installed refractory, ductwork, fans, controls, ladders, platforms, structural, etc.—but excluding plastic feeding and ash removal facilities)  
   $500,000

B. Installation Cost  
   (Includes site preparation, foundations, erection, piping, field wiring, etc.)  
   $500,000

C. Total Investment  
   $1,000,000

D. Income (8600 hrs/yr)  
   Steam value at $6/900 kg ($3/1000 lbs).  
   Savings of 4.5¢/kg (2¢/lb)  
   Total  
   $579,640

E. Expenses  
   Electrical - 100 KW at 3¢  
   Labor - 0.25 operator at $15.00/hr  
   0.25 supervisor at $50,000/yr  
   Depreciation at 10%  
   Maintenance at 3%  
   Miscellaneous  
   Total  
   $220,555

F. Earnings  
   $579,640 - $220,555 =  
   $359,085

G. Gross Return on Investment  
   36%
Obviously, this is a very rough economic analysis, but it should be accurate enough to illustrate that burning waste plastic for steam generation can be a very attractive proposition—especially if environmental authorities permit no alternative.
Table I - Typical Particle Size Distribution of Ash Generated in Hearth Burning of Plastic

<table>
<thead>
<tr>
<th>Particle Size, microns</th>
<th>% by wt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>850 +</td>
<td>0.86</td>
</tr>
<tr>
<td>420 - 850</td>
<td>4.17</td>
</tr>
<tr>
<td>250 - 420</td>
<td>10.54</td>
</tr>
<tr>
<td>150 - 250</td>
<td>27.82</td>
</tr>
<tr>
<td>75 - 150</td>
<td>39.45</td>
</tr>
<tr>
<td>37 - 75</td>
<td>8.0</td>
</tr>
<tr>
<td>19 - 37</td>
<td>4.0</td>
</tr>
<tr>
<td>10 - 19</td>
<td>2.0</td>
</tr>
<tr>
<td>10 and less</td>
<td>3.2</td>
</tr>
</tbody>
</table>
Figure 1 - Block Diagram of Plastics Combustion and Heat Recovery System
Figure 2 - Comparison of Fuel Efficiencies using Various Methods of Cooling Flue Gas prior to Heat Recovery

Temperature (°F) to which flue gas is cooled prior to boiler entry

*Conversion factor: (°K) = 5/9(°F - 32) + 273.15
Figure 3 - Flow Diagram of Combustion and Heat Recovery Process