

Turning mixed plastic wastes into a useable liquid fuel

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As landfill and incineration become more expensive and less accepted, the recycling of plastic wastes is gaining increasing importance. More emphasis is thus being given to new disposal options, which have high energy recovery values and are more environmentally attractive. Pyrolysis is one promising method for the treatment of mixed and contaminated plastic wastes. Plastics are thermally degraded to produce useful liquid hydrocarbons, which can then either be added to existing fuel or solvent product, or returned to a refinery where they can be added to the feedstocks. A simple pyrolysis reactor system is described. Results of pyrolysis tests showed that pure samples of polyolefinic and polystyrene resin can readily be pyrolysed to produce liquid yields in excess of 70%. However, liquid yields were affected by heating rates and heat loss patterns in the reactor system. Further experimental work suggests that when pyrolysed, mixed plastic wastes behave much like the resins from which they originate. In light of the results from the experiments, the technical feasibility of setting up a pyrolysis plant in Victoria to process waste plastics into liquid fuel was discussed. This study thus forms the ground work needed for the design of a small pyrolysis plant.

INTRODUCTION

Recycling of plastics already occurs on a wide scale. Extensive recycling and reprocessing of plastics are performed on homogeneous and contaminant free plastic wastes. However, a substantial fraction of the plastics in municipal waste still ends up in landfills. Minimising the amount of otherwise unrecyclable waste plastics going to landfill is thus the motivation of this research project.

The main hindrance to the implementation of plastics recycling is the inhomogeneity of many plastic wastes. Most recycling schemes require a feedstock that is reasonably pure and contains only items made from a single polymer type, such as high density polyethylene (HDPE) commonly used to make milk bottles or polyethylene terephthalate (PET) soft drink bottles. Realistically, most post consumer wastes contain a mixture of plastic types, and are often contaminated with non-plastic items.

Early research on ways to reuse mixed and contaminated wastes concentrated on mechanical recycling schemes. Such schemes involved melting and then moulding or extruding mixtures of plastic components [1]. Typical products were simple and often bulky items such as walltiles, flowerpots, fenceposts or planks. The wastes processed in this way did not have to be segregated according to plastic type and the presence of limited amounts of small, non-plastic particles was acceptable. A waste processing plant of this kind was established in Melbourne in the late 1980's. Its feedstock was mixed post-consumer plastic wastes and these wastes were converted by melting and extrusion into a material known as Syntal [2], which was marketed as a substitute for more usual construction materials such as concrete and timber.

The disadvantage of such an approach to plastics recycling is that the product no longer has the special characteristics of the plastics used to make it. Thus the product is less useful and ends up competing for markets with cheap construction materials. The presence of non-plastic contaminants leads to concerns from potential buyers about product quality and consistency. For these reasons, mechanical recycling of mixed plastic wastes appears to have only a limited future.

Another widely researched approach to dealing with mixed plastic wastes is incineration. Incineration can be classed as a form of recycling, if carried out with energy recovery. However, incineration is a costly process. Also, if polyvinyl chloride (PVC) is incinerated, HCl is formed and can cause significant corrosion in equipment. An alternative thermal approach to dealing with waste plastics is so-called chemical feedstock or chemical recycling. This term has been used to describe a diversity of techniques, including pyrolysis, hydrolysis, hydrogenation, methanolysis and gasification. Some of these techniques are suitable for use only with homogeneous polymer wastes but others can accept a feed of mixed wastes.

The most attractive technique of chemical feedstock recycling is *pyrolysis*. In its simplest form, this involves heating and decomposing mixed plastics in the absence of oxygen. Unlike mechanical recycling techniques, in which the long polymeric chains of the plastic are preserved intact, pyrolysis produces lower molecular weight fragments. By adjusting operating conditions, the rate and extent of decomposition can be controlled. In this way, it is possible to obtain a predominantly liquid hydrocarbon product with potential for use as a fuel or a refinery feedstock [3]. This approach can be applied to 80% of commodity plastics, so mixed plastic wastes can usually be handled without the need for segregation by polymer type.

Although pyrolysis and related chemical recycling processes have obvious potential, there are still a number of problems. The main one concerns economic viability since the cost of collection and separation of the plastics component in the post-consumer waste stream can be considerable. At a chemical recycling plant in Grangemouth, Scotland, it was found that two-thirds of the operating cost was associated with collection and sorting [4].

Another difficulty relates to plant size and economies of scale. The maximum practical size for a plastics processing plant is determined by the volume of suitable wastes that can be economically collected and transported to the plant. Since the bulk density of plastic wastes is low and the transport costs high, even wastes generated comparatively close to the plant may be uneconomic to recover. Frequently, the quantities that it is cost effective to recover, are well below those needed by an optimally sized plant. In 1995, BASF shelved plans to build a chemical recycling plant in Germany, on the grounds that the German recycling authorities could not provide enough waste plastics to make the project viable [5].

Pyrolysis processes are frequently classified according to their operating temperature [6]. When high yields of liquid hydrocarbons are desired, low temperature (below 550 °C) processes are employed; these yield mainly oils or tars with smaller amounts of gaseous and solid (char) products. As the operating temperature is increased, the gas yield increases and the liquid yield decreases.

Pyrolysis processes can also be classified according to the type of reactor used. Fluidised bed reactors are widely accepted and utilised because they have excellent heat and mass transfer characteristics and maintain a highly uniform temperature across the fluid bed [7]. Under such conditions it is much easier to achieve a desired product mix. A problem with fluidised beds is that they are only viable when run as large-scale units, which are totally unsuited for use in Australia with its widely dispersed population and sprawling urban areas. Waste collection and transport costs would be at least as high as those overseas, and the quantities of waste plastics economically recoverable would almost certainly be smaller.

For Australian conditions, it would be more appropriate to use smaller plants employing a more basic pyrolysis technology. A network of such plants, distributed across the cities and larger regional towns, should enable recovery of a sizeable fraction of the post-consumer waste plastic stream. Ideally, such plants should be able to achieve a good yield of the liquid hydrocarbon product at an acceptable cost. This would need to be suitable for use locally as a fuel or to be sold to the nearest refinery. In the latter case, backloading petrol tankers returning to the refinery could provide a cheap means of transporting the product over quite long distances.

This study is a follow on from the research undertaken by Low *et al.* (1998) [8] which investigated the feasibility of designing a small-scale waste plastics pyrolysis plant. The main problem encountered with the previous experimental setup employing a batch spherical reactor heated with a heating mantle, was the presence of significant charring due to localised heating at the reactor wall. In this study, a more sophisticated experimental design has been developed to better monitor and to allow for greater control of the heating process which influences the products obtained. This paper will report on the technical feasibility of turning mixed plastic waste into a useable liquid product.

EXPERIMENTAL

Materials

The plastics considered in this paper were representative of the major groups of plastics commonly found in municipal wastes. According to the Plastics and Chemicals Industries Association in Australia, plastic packaging (the major plastics component in household wastes) comprises 46% polyolefins (HDPE, LDPE, PP), 44% PET, 6% polystyrene and 4% PVC [9]. However, for reasons as discussed in the previous paper [8], both PET and PVC which did not produce any liquid products, will not be used in the following sets of experiments.

Before examining the influence of additives or contaminants it was necessary to undertake a series of baseline experiments on a representative set of unmodified polymers. These include using pure resin samples of LDPE, HDPE and PS obtained in the form of pellets being 2-4 mm in size. PP was supplied in the form of

atactic-PP solid wax, which was also used to study the effects of varying heating rates on liquid product yield. Tests were also done using typical plastic wastes, derived from discarded HDPE milk bottles, LDPE shopping bags, PP take-away food containers and PS foam cups.

Apparatus and Method

Stage 1: Examined the technical feasibility of pyrolysing plastics into a liquid product. Figure 1 shows the experimental apparatus, which was set up in a fume hood. The design of the apparatus was deliberately kept simple, in line with the aim of the project to develop a recycling approach based on basic technology. The apparatus was designed to operate at low temperatures (below 550 °C) and at atmospheric pressure.

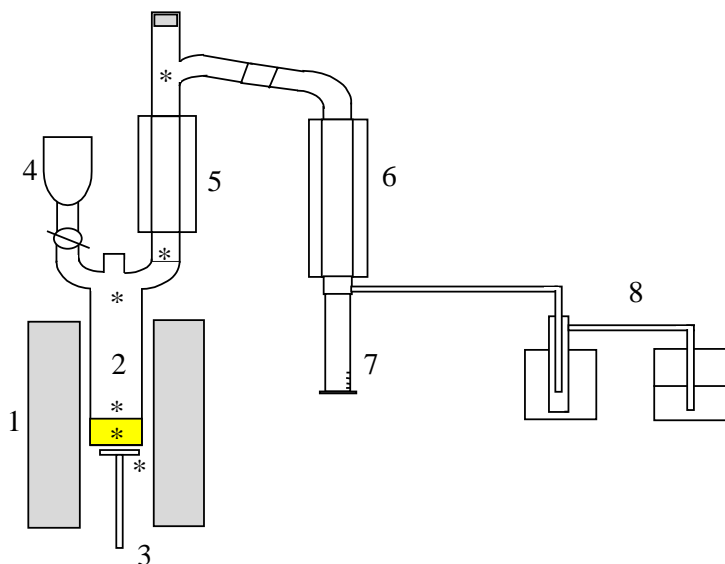


Figure 1 : Experimental setup of pyrolysis reaction system

1 – Tube furnace, 2 – Tubular reactor, 3 – Magnetic stirrer drive, 4 – hopper, 5 – reflux condenser, 6 – product condenser, 7 – liquid collection vessel, 8 – cold trap and ‘*’ – Thermocouple location.

The heart of the experimental apparatus was a vertical tubular reactor (a pyrex tube, 30 cm long by 4 cm in diameter), positioned centrally within a 2.4 kW programmable tube furnace, set at a heating rate of 33°C/min. The reactor was fitted with a magnetic stirrer and a feeder was attached to the reactor’s upper end; this enabled controlled amounts of plastic pellets to be added before or during operation. Vapours leaving the reactor passed into a reflux condenser where higher boiling components were condensed and returned to the reactor for further cracking. Lower boiling components passed through the reflux condenser into a second condenser maintained at 2-5°C and connected to a flask in which the liquid hydrocarbon product was collected. A cold trap was used to minimise the amount of vapour escaping uncondensed from the system. Temperatures were monitored continuously using thermocouples placed as shown in Figure 1; temperatures were recorded at set time intervals using a data logger.

In a typical run, a charge of 40g of the pure resin was placed in a pre-weighed tubular reactor. The reactor was purged with nitrogen and then heating commenced. Heating was continued until evolution of vapours effectively ceased. The furnace was then switched off and the system allowed to cool. The yield of liquid product and the mass of solid residue were found from the increase in weight of the collection flask and the reaction vessel respectively. The mass of gaseous product was found by difference.

Stage 2: Atactic-PP was used as a base case to examine the sensitivity of liquid yields to rates of heating. The method employed is the same as that in Stage 1, except that lower heating rates of 16, 12.5 and 8 °C/min were used.

Stage 3: In this stage, a mixture of selected pure resins and waste plastics were pyrolysed in the following proportion - LDPE 5.8%, HDPE 36.5%, PS 4.8% and PP 2.9%. Experiments were carried out as in Stage 1.

Analytical Procedures

Initially the liquid products were distilled under vacuum into fractions of different boiling range. For each of these fractions, the molecular weight range of the compounds present was determined using gel permeation chromatography (GPC). The liquid products were then analysed using infrared spectrometry (IR) and a gas chromatograph/mass spectrometer unit (GC-MS). The IR analysis provided information on the functional groups present and the GC-MS enabled identification of many of the compounds present and their relative abundance. The GC-MS used was a Jeol AX505H model with a PBX 5 fused silica column; the oven temperature program employed increased the temperature from 30 to 280 °C at 4 °C/min.

RESULTS AND DISCUSSION

The pattern of events typical of these initial runs is best understood by reference to Figure 2. This shows how four key temperatures varied with time over the course of an experimental run. Temperatures were monitored at the following points: in the liquid at the bottom of the reactor; in the vapour above the liquid surface; in the vapour at the inlet to the reflux condenser; and at the vapour outlet from the reflux condenser.

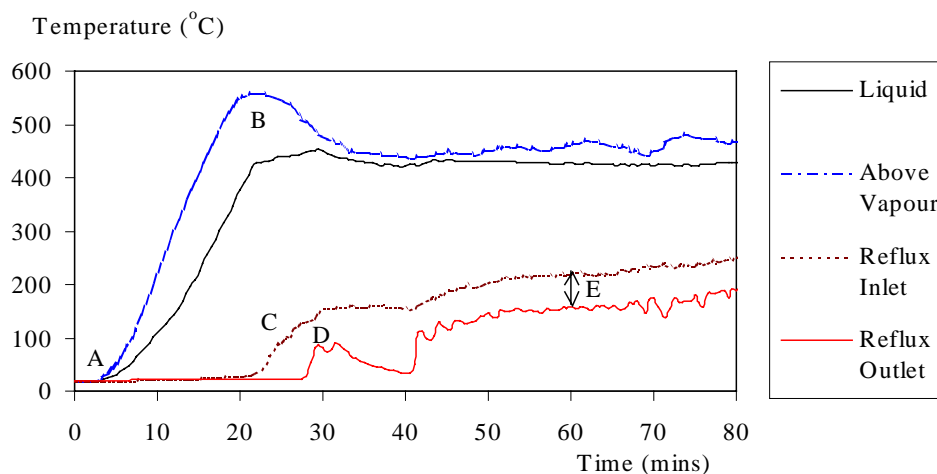


Figure 2. A typical temperature versus time profile (HDPE pyrolysed at 33 °C/min)

For the first few minutes after an experiment is started, temperatures in the reactor system remain unchanged. This is because the furnace is heating up and little energy reaches the reactor. (Transfer of heat to the reactor occurs mainly by radiation.) After 3-4 minutes (point A on Figure 2) heat transfer to the reactor begins and the temperatures in both the liquid and gas/vapour phase sections of the reactor start to increase. Temperatures are higher in the vapour phase as both the vapour and the liquid receive radiant heat from the furnace and the vapour has a much lower thermal mass than the liquid. The difference between the vapour and liquid temperatures reaches a maximum at the point (120-140°C) where the solid polymers melt and considerable energy is taken up in the liquid phase in the form of latent heat.

As vapour temperature peaks at point B, the liquid temperature also reaches the maximum set point temperature. The two temperatures only come together again after point B. This convergence is the result of significant quantities of vapourising from the liquid and displacing the hot vapour from the upper part of the reactor. Beyond point B, both temperatures levels off at a value between 350 and 450°C.

The peak in vapour phase temperature referred to above coincides with a step change in the measured temperature at the reflux condenser inlet (point C); this rises to around 150-200°C, the condensing temperature of small molecular weight hydrocarbon components. This can be attributed to the arrival of vapours, now evolving in quantity from the surface of the liquid. Shortly afterwards some of these vapours reach the outlet of the reflux condenser, where the temperature rises steeply (point D). From around the 30 minute mark, however, it appears as if vapour composition within the reflux condenser undergoes a marked change. The gap denoted by E, between the temperatures at the inlet and outlet ends of the reflux condenser shows that components with a wide range of boiling points are present; the slight drop in outlet temperature suggests that vapour flowrates through the system are decreasing and that a substantial fraction of the incoming vapour is being condensed and returned to the reactor for further cracking. The temperature at the

outlet of the reflux condenser, and the size of the gap denoted by E both change if the heat duty of the reflux condenser is altered.

The yields of liquid, gas and residual products for a number of the pure resins analysed in Stage 1 are shown in Table 1. These results showed that a-PP, HDPE, LDPE and PS were readily pyrolysed to yield in excess of 70% by mass of liquid product. In all cases these liquid products were clear, with viscosities of 0.70-0.75 centipoise at 38°C and specific gravities of 0.75-0.80. The residue in the flask was waxy in nature and contained a small percentage of char.

Table 1. Product yields for pyrolysis of pure thermoplastic resins.

| SAMPLES | PRODUCT YIELD | | |
|---------|---------------|-----------|---------------|
| | Liquid (wt%) | Gas (wt%) | Residue (wt%) |
| a-PP | 77 | 22 | 1 |
| HDPE | 70 | 28 | 2 |
| LDPE | 73 | 10 | 16 |
| PS | 80 | 17 | 7 |

IR analyses showed that as expected, the liquid product from polyolefins consists primarily of alkanes and alkenes. Polystyrene gives similar compounds but, not unexpectedly, there were some aromatics. GC-MS results confirmed alkanes and alkenes mainly in the C₉ to C₂₅ carbon number range and the presence of aromatics including styrene, toluene and xylene were present in the liquids formed from polystyrene.

Result of analysis of the liquid products from Stage 1 were most encouraging as they conform to those in the main hydrocarbon products from refineries. For example, typical carbon numbers of some important products include petrol, C₄ to C₁₂; kerosene, C₁₀ to C₁₈; diesel, C₁₅ to C₂₅; fuel oils, C₂₀ to C₅₀. This suggested that the products produced by pyrolysis should be suitable either for adding to existing fuels or as intermediate feedstock to a refinery.

Stage 2 results as indicated in Table 2, suggests that liquid yield decreases while gaseous yield increases as lower heating rates were applied. This indicates that to obtain a useful product mix it will be necessary to use high heating rates.

Table 2. Sensitivity of product yields to different rates of heating.

| HEATING RATE (°C / min) | PRODUCT YIELD | | |
|----------------------------|---------------|-----------|---------------|
| | Liquid (wt%) | Gas (wt%) | Residue (wt%) |
| 33 | 77 | 22 | 1 |
| 16 | 66 | 28 | 6 |
| 12.5 | 64 | 32 | 4 |
| 8 | 55 | 41 | 4 |

In Stage 3, a limited number of experiments were performed using resins mixed in proportions expected in household waste. Results showed that while the liquid product compositions were very similar (between C₉ and C₂₅), the liquid yields for the mixed waste portions were slightly lower than those obtained for pure resins. Further investigation is needed in this area, however there is potential that with process optimisation these yields may improve.

CONCLUSION

It has been shown that a simple batch pyrolysis method can convert polyolefins and polystyrene to liquid hydrocarbon products with a yield of at least 70%. Preliminary tests using mixed waste plastics were promising and confirmed the feasibility of converting such wastes to liquid products. These liquid products have compositions overlapping those of major existing hydrocarbon fuels such as petrol, diesel and kerosene. Use of these products directly as a fuel or for reprocessing in a refinery therefore appears possible. The study performed in this paper has provided important information showing that prospects for using small-scale simple pyrolysis processes to deal with waste plastics appear good but further investigations are required.

Such investigations should include ways to exclude or remove PET and PVC from mixed plastic wastes; establishing the extent to which patterns of thermal decomposition of plastic mixtures conform to those of the

individual polymers present; and elucidation of the impact of additives and/or contaminants on the ways in which plastic mixtures decompose.

NOMENCLATURE

| | |
|------|----------------------------|
| a-PP | atactic polypropylene |
| HDPE | high density polyethylene |
| LDPE | low density polyethylene |
| PET | polyethylene terephthalate |
| PS | polystyrene |
| PVC | polyvinyl chloride |

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REFERENCES

1. Hegberg, B. A., Brenniman, G.R., Hallenbeck, W.H., (1992), *Mixed Plastics Recycling Technology*. Noyes Data Corp. New Jersey.
2. Australian and New Zealand Environmental Council (1990), Plastic waste and the economic potential for recycling, pp. 31, Technisearch Ltd.
3. Mader, F., Mennicken, T., (1995), The Feedstock Option. *Shell Chemicals Europe Magazine*, 20-23.
4. Lascelles, D. (1994), Place for Plastics, pp. 18: *Financial Times*.
5. Anon (1995), BASF Shuttles Plastic Feedstock Recycling Plant. *Chemical Market Reporter*, 7.
6. Buekens, A. G., Schoeters, J.G., (1980), Basic Principles of Waste Pyrolysis and Review of European Processes, pp. 398-421. In J. L. James, Radding, S.B., (Ed.): *Thermal Conversion of Solid Wastes and Biomass*, American Chemical Society, Washington.
7. Kaminsky, W. (1995), Pyrolysis with respect to recycling of Polymer. *Die Angewandte Makromolekular Chemie*, **232**, 151-165.
8. Low, S. L., Connor, M.A., Covey, G.H. (1998), The feasibility of using pyrolysis to convert contaminated municipal thermoplastic waste to liquid fuel, pp. 269-276. In M. Sivakumar, Chowdhury, R.N. (Ed.): *Environmental Management : Engineering the Water-Environment and Geo-Environment (Proc. Second International Conference on Environmental Management, Wollongong, Australia, 10-13 February 1998)*, Amsterdam.
9. PACIA (1994), Report for Plastics and Chemicals Industries Association, SIRA International.