THERMAL AND PYROLYTIC PROCESSES FOR THE VALORIZATION OF WASTE PLASTICS

Paul T. Williams

Energy & Resources Research Institute, The University of Leeds, Leeds LS2 9JT, UK
e-mail: p.t.williams@leeds.ac.uk

Abstract

Waste plastics are produced in various municipal and industrial waste streams. Each waste stream presents particular problems for feedstock recycling, however, each stream also offers potentially great benefits in terms of not only plastic waste feedstock recycling, but for the recovery of other high value fractions from the waste. This paper describes the application of thermal and pyrolytic processes for the recycling of various plastic wastes including mixed plastic waste from municipal solid waste, waste electronic & electrical equipment, and composite plastic wastes. Examples of the recycling of the plastic waste streams are presented in relation to the recovery of oils for feedstock recycling, synthesis gas/hydrogen for fuels and solid materials recovered from the waste feedstock.

Keywords: *MSW; WEEE; Printed Circuit Boards; Composites; Hydrogen*

1. Introduction

Approximately 230 million tonnes of plastics are produced worldwide each year with European production representing more than 50 million tonnes [1]. It is estimated that only about 50% of the plastics produced in Europe each year are available for collection and recycling, the remainder accumulating in the environment as long term uses of plastics such as building works, including, plastic window frames, pipes, electrical wiring, etc. Of this collectable waste plastic, only about 5.5 million tonnes, is recycled with the remainder incinerated with other wastes, mainly as municipal solid waste, or is disposed of, mostly to landfill. Recycling is dominated by mechanical routes to produce low grade products. The low grade uses for plastic recycled materials has led to research into alternative processing methods to produce higher value products. One example is via feedstock recycling where the plastic waste materials are processed back to produce basic petrochemicals that can be used as feedstock to make virgin plastic. Pyrolysis of plastics, thermally degrades the plastic, breaking the bonds of the polymer to produce lower molecular weight oligomers and monomers.

Plastic waste occurs in a variety of waste streams, including, mixed plastic waste from municipal solid waste, waste electronic and electrical equipment, and composite plastic wastes. The plastic component of the waste can be recycled by pyrolysis to produce an oil for use as a petrochemical feedstock and also a gas to provide the energy requirements of the pyrolysis process. In addition, the plastic can be gasified using catalytic steam gasification to enhance the production of synthesis gas. Some of the plastic waste types contain additional material that can be recovered, for example, waste electrical and electronic waste contains printed circuit boards where valuable metals can be recovered, composite plastic materials contain valuable glass or carbon fibres which can be recovered. This paper presents thermal and pyrolysis processes for a variety of waste plastics for the recovery of oils for feedstock recycling, synthesis gas/hydrogen for gaseous fuels and higher value solid materials.

2. Waste Plastic Materials and Processes

2.1. Municipal solid waste

The six main plastics in municipal solid waste are thermoplastics consisting of, high density polyethylene (HDPE), low density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC) and polyethylene terephthalate (PET). The product yield from pyrolysis is related directly to the type of plastic, the reactor type and the process conditions, particularly pyrolysis temperature. Pyrolysis of plastics produces an oil/wax product. The distinction between the yield of condensed hydrocarbon wax and oil is a consequence of the pyrolysis reaction system, temperature, condensation collection system and condensation temperature. For example, fluidised bed pyrolysis of various plastics at 550 °C in a fluidised bed reactor with rapid cooling of the condensate using water cooled condensers produced an oil/wax ratio of 1.23 for HDPE, 0.50 for LDPE, 0.82 for PP, 4.75 for PS and 1.48 for PET [2]. In addition, it was shown that PVC produced 100% oil and no wax [2]. Polyethylene has been pyrolysed in a fluidised bed reactor at 530 °C and an oil yield of 50.3wt% and a wax yield of 42wt% was reported [3]. Vacuum pyrolysis of various plastics produced 88wt% conversion of LDPE to wax and 8wt% to an oil. For HDPE, the conversion was 92.3wt% to wax and 5.4wt% to oil, for PP the conversion to wax was 70wt% and 25wt% oil [4]. It was also shown that when polystyrene was pyrolysed in the vacuum reactor, 58.6wt% light oil was produced and 40.7wt% heavy oil [4].

Further developments in the process of feedstock recycling of plastics have included the use of catalysts. The use of a catalyst has been proposed as a way of producing a high aromatic product for the production of gasoline or as a chemical feedstock or for the production of speciality chemicals. Catalysts can reduce the required reaction temperature, improve the yield of volatile products and provide selectivity in the product distributions. Different catalyst types can alter the temperature of thermal degradation of the plastic and could also be used to define the composition. For example, pyrolysis of a number of plastic types over a zeolite ZSM-5 catalyst has shown that the use of a catalyst increased the aromatic content of the derived product oil [5].

The gasification of plastics produces a syngas which has a high content of hydrogen. Hydrogen has been identified as a fuel which might play an important role in future energy supplies. Czernik and French [6] have demonstrated the potential of the gasification process for plastics to produce hydrogen. Different process conditions such as gasification temperature, introduction of a catalyst and introduction of steam etc. have an influence on the production of hydrogen from the gasification of plastics [7,8]. A key factor in maximising the production of hydrogen from waste plastics using pyrolysis-gasification is the use of catalysts. Nickel catalysts are commonly used in the gasification process due to their lower price and effective catalytic activity. Furthermore, in order to obtain high concentrations of hydrogen in the product gases, multiple stage reaction systems have been applied to the gasification process [7,8].

2.2. Waste electrical & electronic equipment (WEEE).

Total electrical and electronic equipment waste generated in the European Union have been estimated at approximately 10 million tonnes per year. Pyrolysis of three plastic fractions from a commercial waste electrical and electronic equipment (WEEE) processing plant have been investigated [9]. The plastic waste included material from equipment containing cathode ray tubes, from refrigeration equipment, and from mixed WEEE. The major pyrolysis product of each plastic was pyrolysis oil with only small amounts of gas being produced. Each of the pyrolysis oils was characterised by GC-MS, which showed that all the oils contained mainly aromatic compounds and both nitrogenated and oxygenated compounds. The pyrolysis oils contained very few organic halogens and it was also reported that the real-world waste samples of WEEE plastic had low halogen content. It has been reported that only 2.5% of WEEE plastic contains halogens, usually in the form of brominated flame retardants [9].

Virtually all electrical and electronic equipment contain printed circuit boards. Printed circuit boards are particularly problematic to recycle because of the heterogeneous mix of organic material, metals, and glass fibre and low recycling rates are reported of about 15% [10]. It has been estimated that a typical printed circuit board is composed of 40 wt% metals, 30 wt% plastics and 30 wt% of ceramic material. The metals present include large amounts of copper, aluminium and iron, but also precious metals such as gold, silver and palladium which increase the interest in recycling technologies to recover such metals. In addition, the plastic fraction of the printed circuit board represents an important fraction to meet recycling and recovery targets.

Pyrolysis of printed circuit boards has been an area of extensive research. De Marco et al [11] pyrolysed printed circuit board waste produced from a WEEE recycling plant. The product yield from pyrolysis, produced 76.5 wt% solid residue, 16.2 wt% oil and 7.3 wt% gas. The solid residue consisted of 5.8 wt% char derived from the pyrolysis of the epoxy resin and the metals and ceramic materials. The pyrolysis liquid oil was composed of products related to the original polymer of the plastic fraction, being mainly epoxy resin which produced a pyrolysis oil of mainly aromatic oil of low viscosity containing high concentrations of phenol and phenol derivatives. Pyrolysis gases were composed of mainly hydrocarbons from C_1 – C_5 consisting of mainly ethane and ethane and also CO and CO_2. The pyrolysis of printed circuit boards derived from waste computers, televisions, and mobile telephones has been reported [12]. The pyrolysis gases consisted mainly of CO_2 and CO and C_1 – C_4 gases and some inorganic bromine was also present, inorganic chlorine was also present in the mobile telephone printed circuit board pyrolysis gas. The pyrolysis oils contained high concentrations of phenol, 4-(1-methylethylphenol), and p-hydroxyphenol, which are all regarded as decomposition products of epoxy resins. After pyrolysis, the metals and pyrolysis char can be easily separted, either by mechanical separation or mild oxidation. The metals consist of copper in high concentration with high concentrations of calcium, iron, nickel, zinc, aluminium, lead, and silver also found in most of the residues.

2.3. Composite plastic waste.

Advanced composite materials offer a combination of high strength, lightness and corrosion resistance that have made them increasingly popular in the manufacturing industries Fibre reinforced composite plastics, comprising thermoset or thermoplastic polymer matrices with glass, carbon and/or polymer fibre reinforcement, offer a combination of strength, durability, low weight and corrosion resistance that has made them increasingly important products, especially in the automotive vehicle sector. Thermoset unsaturated polyester resins are employed in the manufacture of glass-reinforced polyester (GRP), sheet moulding compound (SMC) and dough moulding compound (DMC), extensively used in the production of automotive vehicles. When the vehicle reaches the end of its life it has to be scrapped and it has been estimated that the number of end-of-life vehicles will reach almost 19 million cars in Western, Central and Eastern Europe by 2015.

However, the complex nature of composite materials, coupled with the thermoset resins used, presents major problems to recycling and much of the composite waste currently produced must ultimately be disposed of via landfill

As a process for recycling fibre-reinforced composite plastic waste, pyrolysis has the advantage that all of the products can potentially be recovered and reutilised in one form or another. The polymeric components decompose to produce potentially useful oil and gas products, and controlled pyrolysis enables the recovery of the fibre reinforcement with minimum degradation. The recovered fibres could then be recycled back into the composite production industries.

Pyrolysis of a thermoset polyester/styrene copolymer reinforced with glass fibre has been pyrolysed at 450°C [13]. The main gases evolved were CO and CO_2, which accounted for more than 75vol % of the total gas composition. Other gases identified were H_2, CH_4 and other hydrocarbons from C_2-C_4. The properties of the pyrolytic oil, including calorific value, viscosity and elemental analysis, suggested that it could be a viable liquid fuel. The condensable products could also be a valuable source of chemical feedstocks including styrene and phthalic anhydride, which could potentially be recycled into polyester/styrene resins. The pyrolysis process produced a solid char, filler and glass fibres. The glass fibres could be easily separated from the pyrolysis char and filler and could be recycled to produce new composite plastic material. The glass fibre recovered from the solid residue had mechanical properties which showed that they could replace up to 20wt% of virgin glass fibre in Dough Moulding Compound (DMC).

Carbon fibre reinforced plastics comprising thermoset and thermoplastic polymer matrices, are considered as one of the most attractive products due to their strength, durability, low weight and corrosion resistance and are commonly used in the aerospace and automotive sectors. Carbon fibres are regarded as high value products and their recovery from the composite waste via pyrolysis is economically attractive. Carbon fibre composite waste composed of carbon fibres and polybenzoxazines resin has been pyrolysed in a fixed bed reactor at temperatures between 350 and 700 ºC [14]. Solid residues of between 70-83.6 wt%, liquid yields 14-24.6 wt% and gas yields 0.7-3.8 wt% were reported depending on pyrolysis temperature. The derived pyrolysis liquids contained aniline in high concentration together with oxygenated and nitrogenated aromatic compounds. The pyrolysis gases consisted mainly of CO_2, CO, CH_4, H_2 and other hydrocarbons. The carbon fibres used in the composite waste were separated from the char of the solid residue via oxidation and investigated for their mechanical strength properties. The recovered carbon fibres exhibited mechanical properties which were 90% of that of the original virgin carbon fibres.

3. Conclusions

Many types of plastic waste can be recycled using thermal and pyrolyitic processes to produce high value fuels, chemical feedstocks, gases, hydrogen, or for the recovery of solid materials such as high value metals or glass/carbon fibres from the waste. The influence of process conditions can be used to determine the yield and composition of the product stream or the optimised recover process for the targetted end-product.

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