

Pyrolysis of Carbon-based Waste Materials – A Review

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Introduction

In the UK there is increasing pressure to reduce the quantity of municipal solid waste (MSW) being sent to landfill sites for disposal [1], and thermal treatments, including energy conversion, are increasingly being viewed as a potential solution [2]. The composition of municipal solid waste shows considerable variations, mainly influenced by socio-economic, geographical and seasonal factors [2,3,4], and upgrading of waste to produce refuse-derived fuel (RDF) for power generation is now an established practice [5].

However, from a materials viewpoint, disposal by burning in air is wasteful, because a valuable source of carbon-based materials, which could be exploited to achieve more efficient use of resources, is lost. Furthermore, the main components of MSW, comprising both synthetic polymer and cellulose-based materials, lend themselves to a variety of other potential solutions, including reprocessing by pyrolysis [2], with the several products of the process forming an integral part of a potential renewal cycle. This paper presents a brief review of the recent literature relating to pyrolysis of organic carbon-based materials that might contribute to a sustainable cycle of design, manufacture, re-use and/or regeneration.

The Pyrolysis Process

Pyrolysis involves the thermal breakdown of organic waste in the absence of oxygen to produce a complex mixture of molecular structures that contribute to useful end products in the form of condensable oily liquids, volatile gases and carbonaceous char residues. The process is endothermic, so a source of external heat is required. This can often be provided as a by-product, as the lighter gaseous fraction can have a sufficiently high calorific value to provide the heat for the pyrolysis process and pre-drying of the waste, if required [e.g. 6]. Processing temperatures are relatively low, typically in the range 400-800°C, and a range of environments can be used, e.g. self-generated, inert gas, steam, or vacuum. The processing conditions can be varied to maximize the production of a particular fraction, but all components of the degradation process are potentially useful. The liquid fraction can be processed to produce a range of chemicals for use either as refined fuels or as chemical feedstock [7,8], and the char either burnt as a solid fuel or processed into carbon black or upgraded to activated carbon [e.g. 9].

Of all the available waste treatment processes, only pyrolysis provides a viable method for the recovery of useful products from the whole of the waste stream without the need for prior separation of the organic components. All organic waste, including food waste, garden waste, paper and plastics can be co-processed. It should be noted, however, that the liquid product from pyrolysis of biomass contains significant

amounts of water, and the oily component is high in oxygen-containing compounds, both of which can affect its value as a fuel. Furthermore, the oily product is frequently highly acidic and suffers from chemical instability during storage [10]. Consequently, a significant amount of subsequent processing is required to optimize the yield of useful chemicals.

Products of Thermal Decomposition of Organic Wastes

Three principal fractions are obtained from controlled pyrolysis of organic materials in an oxygen-free environment: gaseous (simple gases and low molecular weight non-condensable compounds), condensable volatile liquids (aqueous, oils, waxes) and solid residues (tars, char, ash). These are produced in different proportions, depending on the source material, and the conditions of temperature, atmosphere, heating rate and residence time. The published results from a number of laboratory bench and larger scale experiments, including several specialist pyrolysis facilities [11], have been collated from the literature. Woody biomass materials containing cellulose, hemicellulose (xylan) and lignin have received particular attention in recent years, as have common synthetic polymers, some mixed wastes and rubber from waste tyres. Pyrolysis data for these common waste components have been summarised in the form of ternary 'product maps' to illustrate the effects of the main variables on the principal fractions obtained. An example for biomass is shown in Figure 1.

In the case of natural biological materials containing cellulose, pyrolysis is usually carried out in batch reactors at moderate heating rates (10°C/min) with process temperatures in the region of 400-600°C. Pyrolysis under these conditions is normally referred to as 'conventional' or 'slow' pyrolysis. Lower temperatures (<400°C) and slow heating rates (a few degrees per minute) for long times (hours) favour the production of solid char residues, akin to the production of charcoal from wood. High temperatures (up to 800°C) assist the breakdown of larger molecules into simpler ones, producing a larger gaseous fraction. In contrast, high heating rates (up to 1000°C/sec) in specialist facilities with very short residence times (<1 sec), combined with rapid cooling of the vapour phase, minimise thermal decomposition and secondary reactions giving a predominantly liquid product. These conditions are generally referred as 'fast' or 'flash' pyrolysis, and frequently involve fluidized bed, gas entrainment, recirculated sand or ablative methods of achieving high heat transfer rates to small particles of the feed material.

Yaman [8] has provided a comprehensive review of the extensive literature published during the 1990s pertaining to the production of fuels and chemical feedstocks from a range of biomass sources, including those derived from herbaceous plants, wood waste, bagasse, waste paper, MSW, animal wastes and food processing wastes. Catalysts can be used directly to improve yields, and particularly the characteristics, of pyrolysis oils. The potential to upgrade bio-oils in respect of calorific value by use of catalysts and by steam reforming has been extensively examined [e.g. 8,12,13,14].

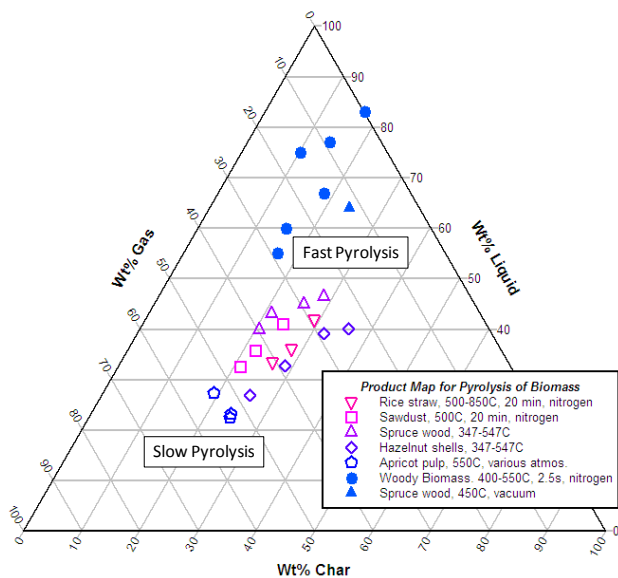


Fig. 1 Example of Product Map for Pyrolysis of Biomass.

A range of complex reactions occurs during pyrolysis involving different mechanisms and chemical pathways through the formation of organic radicals. Consequently, the liquid fraction obtained from the pyrolysis of biomass contains a mixture of aliphatic, aromatic and polar compounds, many of which are highly oxygenated, including acids, alcohols (including methanol), aldehydes, ketones, esters and phenolics [15,16]. The gas phase is a mixture of low molecular weight volatile compounds, rich in carbon dioxide, carbon monoxide, methane, hydrogen, ethane, ethene (ethylene) and water vapour. In the case of fast pyrolysis of biomass, the reactor configuration and the dominant mode of heat transfer strongly influence the average molecular weight of the products [7]. The solid residue from pyrolysis of biomass contains carboniferous char, residual material and ash, the ash content commonly ranging from 1wt% to 15wt%. The physical properties of the char can vary widely, depending on the pyrolysis conditions, but, if prepared with a suitable pore structure and internal surface area, it can be used for the production of activated carbon. These characteristics are best achieved using fast pyrolysis.

In many respects the thermal decomposition of common plastics and rubbers is less complex than biomass. The pyrolytic decomposition of polyethylene, polypropylene (PP), polystyrene (PS) and polyethylene terephthalate all occur as single stage processes over a range of temperature in nitrogen or vacuum. Liquid yields are shown to increase with the use of catalysts [17]. In the case of PP and PS, the main products are liquid, with PS yielding a high proportion of styrene monomer [18,19].

Cunliffe et al. [20] have studied the thermal decomposition behaviour of a range of reinforced polymer composite materials containing glass and/or carbon fibres. Samples containing various resins and PP, were pyrolysed over the temperature range 350-800°C. It was noted that reinforcing fibres can be recovered from composite residues,

albeit with impaired properties. Potential uses include recycling into new composites or incorporation into concrete.

Discussion and Conclusions

This brief review has identified a range of organic materials that, potentially, could form the basis of a sustainable renewal cycle, possibly including novel carbon-based composite materials. Such a cycle could include products specifically designed for recycling at end of life using pyrolysis, combined with energy recovery.

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