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Review

Pyrolysis of waste tyres: A review

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ABSTRACT

Approximately 1.5 billion tyres are produced each year which will eventually enter the waste stream representing a major potential waste and environmental problem. However, there is growing interest in pyrolysis as a technology to treat tyres to produce valuable oil, char and gas products. The most common reactors used are fixed-bed (batch), screw kiln, rotary kiln, vacuum and fluidised-bed. The key influence on the product yield, and gas and oil composition, is the type of reactor used which in turn determines the temperature and heating rate. Tyre pyrolysis oil is chemically very complex containing aliphatic, aromatic, hetero-atom and polar fractions. The fuel characteristics of the tyre oil shows that it is similar to a gas oil or light fuel oil and has been successfully combusted in test furnaces and engines. The main gases produced from the pyrolysis of waste tyres are H_2, C_1–C_4 hydrocarbons, CO_2, CO and H_2S. Upgrading tyre pyrolysis products to high value products has concentrated on char upgrading to higher quality carbon black and to activated carbon. The use of catalysts to upgrade the oil to a aromatic-rich chemical feedstock or the production of hydrogen from waste tyres has also been reported. Examples of commercial and semi-commercial scale tyre pyrolysis systems show that small scale batch reactors and continuous rotary kiln reactors have been developed to commercial scale.

1. Introduction

It is estimated that 1,500,000,000 tyres are produced worldwide each year which will eventually end-up as waste tyres (ETRMA, 2011). In terms of tonnages, waste tyres represent a significant proportion of the total solid waste stream. For example, approximately 3.3 million tonnes of waste tyres were generated annually within Europe (EU-27) in 2010 and an estimated stockpile of 5.7 million tonnes of waste tyres throughout Europe (ETRMA, 2011). The management of waste tyres in the European Union has been regulated under the End of Life Vehicle Directive which stipulates the separate collection of tyres from vehicle dismantlers and encourages the recycling of tyres (EC, 2000). In addition, the EU Waste Landfill Directive has banned the landfilling of tyres (EC, 1999). These Directives have dramatically changed the tyre waste treatment routes in the EU over the last 15 years. For example in 1996 approximately 50% of waste tyres were sent to landfill, however, currently the figure is only 4% (0.13 million tonnes/year) (ETRMA). The main options used for treating waste tyres are through the use of tyres as fuel in cement kilns which accounts for more than 1.15 million tonnes of the total 3.3 million tonnes of waste tyres generated each year in the EU (ETRMA, 2011). Other energy recovery options for tyres include use in power plants and co-incineration with other wastes which use approximately 0.1 million tonnes per year of tyres. About 1.1 million tonnes of tyres are used in material recovery options through the production of rubberised flooring in sports fields and playgrounds, paving blocks, roofing materials, etc. A significant proportion of the waste tyres are used in civil engineering applications such as road and rail foundations and embankments (0.24 million tonnes) re-treaded (0.26 million tonnes) or exported (0.33 million tonnes) each year (ETRMA, 2011). Sienkiewicz et al. (2012) have extensively reviewed the waste treatment routes for waste tyres in the European Union and its Member States and the possible uses of waste tyres as a source of raw materials or alternative fuels.

Typical compositions of passenger and truck tyres are shown in Table 1 (Evans and Evans, 2006). The rubbers and elastomers which make up the rubber component of the tyre are a mixture of several rubbers strengthened with carbon black filler material. The construction of the tyre involves a composite of several layers of the rubber, textile material and steel belt and cord.

There has been great interest in alternative treatment processes for waste tyres, amongst which is the use of pyrolysis technology (Sienkiewicz et al., 2012). Pyrolysis is the thermal degradation of the organic components of the tyres, at typical pyrolysis temperatures of 500 °C to produce an oil, gas and char product in addition to the recovery of the steel. The oil may be used directly as a fuel, added to petroleum refinery stocks, upgraded using catalysts to a premium grade fuel or used as a chemical feedstock. The gases from tyre pyrolysis are typically composed of C_1–C_4 hydrocarbons and hydrogen with a high calorific value, of sufficient energy content to act as fuel to provide the heat for the pyrolysis process. The solid char consists of the carbon black filler and also char

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Table 1
Typical composition of passenger and truck tyres (Evans and Evans, 2006).

Component	Passenger tyre (wt.%)	Truck tyre (wt.%)	Comments
Rubber	47	45	Many different synthetic and natural rubbers are used, e.g. styrene–butadiene rubber, natural rubber (polyisoprene), nitrile rubber, chloroprene rubber, polybutadiene rubber
Carbon black	21.5	22	Used to strengthen the rubber and aid abrasion resistance
Metal	16.5	21.5	Steel belts and cord for strength
Textile	5.5	–	Used for reinforcement
Zinc oxide	1	2	Used (with stearic acid) to control the vulcanisation process and to enhance the physical properties of the rubber
Sulphur	1	1	Used to cross link the polymer chains within the rubber and also to harden and prevent excessive deformation at elevated temperatures
Additives	7.5	5	e.g. Clay or silica used to partial replacement carbon black

produced during the pyrolysis of the rubber. It may be used as a solid fuel, as carbon black or upgraded to produce an activated carbon.

In this paper, the pyrolysis of tyres is reviewed in terms of the range of pyrolysis reactors used. The influence of process parameters, on the yield and composition of the products from the pyrolysis of tyres are discussed. The fuel properties of the oils and their detailed chemical composition are discussed, the characteristics of the chars and gas composition is presented in detail. The research related to producing higher value products from the tyre pyrolysis process is also reviewed. The range of pyrolysis reactors at the commercial and semi-commercial scale are also discussed.

2. Pyrolysis reactors and product yield

A range of different reactors, such as fixed-bed (batch), screw kiln, rotary kiln, vacuum and fluidised-bed have been used for pyrolysis of waste tyres. Table 2 shows the range of pyrolysis reactors used to research the pyrolysis of waste tyres and the yields of oil, char and gas from the process. In some cases, the data include the recovery of the steel belt and cord which typically ranges from 10 to 15 wt.% of the waste tyre. Fixed bed, batch reactors have been widely used to investigate pyrolysis of waste tyres. The reactor is typically heated externally by an electric furnace and nitrogen or another inert gas is used as a carrier gas. The thermally degradation of the tyre starts at around 350 °C and therefore pyrolysis experiments are usually in the range of 450–700 °C. The derived gas products are carried by the carrier gas and condensed downstream and the non-condensable gases are collected and analysed. The residual char and any steel are collected after experimentation. Although there are some commercial fixed bed batch reactors for processing tyres (see Section 7), the desire for a continuous process has led to investigations of rotary kilns, moving bed screw reactors and fluidised beds. In such systems the waste tyre is fed directly to the hot reactor.

2.1. Fixed bed reactors

Aydın and Ilkılıc (2012) investigated the pyrolysis of waste tyres, with steel and fabric removed, in a 1.15 l capacity fixed bed reactor in nitrogen over the temperature range of 400–700 °C. They found that the oil yield increased from 31 wt.% at 400 °C, increasing to 40 wt.% at 500 °C, with little change in yield at higher temperatures. There was a consequent increase in gas yield. They also investigated the influence of nitrogen flow rate on product yield and found only negligible differences in yield. Williams et al. (1990) used a small scale, fixed bed, batch reactor to investigate the influence of pyrolysis temperature from 300 to 720 °C and heating rate from 5 to 80 °C min^{-1} on product yield from the pyrolysis of ~50 g of tyre. At the low temperature of 300 °C there was little thermal degradation of the tyres. To maximise oil yields of between 54 and 58.8 wt.%, pyrolysis temperatures of 600–720 °C were required. It should be noted that raising the temperature in a fixed bed reactor system beyond where the rubber has been thermally degraded only marginally increases the yield of oil and gases. These oils and gases are most probably produced from the volatilisation of some of the solid, very higher molecular hydrocarbon content of the char (Dodds et al., 1983).

Using a larger fixed bed reactor with a feedstock loading of 1.5 kg and a pyrolysis temperature of 475 °C and heating rate of 5 °C min^{-1} Cunliffe and Williams (1998a) obtained yields of oil, char and gas at 58.2 wt.% oil, 37.3 wt.% char and 4.5 wt.% gas. Islam et al. (2011) using a fixed bed reactor pyrolysed 750 g batches of waste tyre and also found a high oil yield of 55 wt.% at 475 °C pyrolysis temperature with a corresponding char and gas yield of 36 wt.% and 9 wt.% respectively. Kar (2011) pyrolysed 10 g batches of waste tyres in a fixed bed, nitrogen purged reactor at 10 °C min^{-1} heating rate. The influence of pyrolysis temperature from 375 to 500 °C was investigated and it was reported that the maximum oil yield of 60.0 wt.% oil was obtained at 425 °C. At the higher temperature of pyrolysis, of 500 °C, the oil yield decreased to 54.12 wt.%. The gas yield increased from 2.99 to 20.22 wt.% and char yield decreased from 50.67 to 26.41 wt.% as the temperature of pyrolysis was increased from 375 to 500 °C. However, for similar pyrolysis conditions, Banar et al. (2012) reported that for pyrolysis of tyre derived fuel (steel removed) the maximum oil yield was only 38.8 wt.%, with char yield at 34 wt.% and a high gas yield of 27.2 wt.% for a heating rate of 5 °C min^{-1} at a pyrolysis temperature of 400 °C. A similar oil yield of 38.0 wt.% at the pyrolysis temperature of 500 °C and 15 °C min^{-1} heating rate was obtained by Laresgoiti et al. (2004) and de Marco et al. (2001). Rada et al. (2012) also obtained an oil yield of 40 wt.% and gas yield of 20 wt.% and char yield of 40 wt.% for the fixed bed batch pyrolysis of tyres. Differences in heating rates and in particular pyrolysis gas residence times can significantly impact the relative yields of oil and gas, where higher temperatures of pyrolysis and long gas residence times in the hot zone of the reactor can crack the oil to gas.

Williams et al. (1990) reported that increasing the heating rate showed an increase in gas yield, being 6.6 wt.% at 5 °C min^{-1} heating rate which increased to 14.8 wt.% gas at 80 °C min^{-1} heating rate, where both experiments were undertaken at 720 °C pyrolysis temperature. Banar et al. (2012) reported a significant influence of heating rate, where oil yield decreased to 35.1 wt.% and gas yield increased to 33.8 wt.% as the heating rate was increased from 5 to 35 °C min^{-1} at the pyrolysis temperature of 400 °C. The influence of very fast heating rates of 1200 °C min^{-1} have been investigated over a temperature range of 500–1000 °C (Leung et al., 2002). It was shown that under such high heating rate conditions, the gas yield increased from 5.0 wt.% at 500 °C to 23 wt.% at 900 °C.

Large batch reactor systems processing around 1 tonne of whole and shredded waste tyres have reported lower yields of oil for example, 20.9 wt.% oil (24.0 wt.% oil, corrected for steel) and