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.

Key words: Review; Tyres; Pyrolysis; Oil; Char; Gas

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 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 form 10-15 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

Aydin and Ilkilic (2012) investigated the pyrolysis of waste tyres, with steel and fabric removed, in a 1.15 litre 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 °C min^{-1} to 80 °C min^{-1} on product yield from the pyrolysis of ~50g of tyre. At the low temperature of 300 °C there was little thermal degradation of the tyres. To maximise oil yields of between 54 wt.% 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 ºC min^{-1} heating rate. The influence of pyrolysis temperature from 375 – 500 ºC was investigated and it was reported that the maximum oil yield of 60.0 wt.% oil was obtained at 425 ºC. At the higher temperature of pyrolysis, of 500 ºC, 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 – 500 ºC. 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 °C min^{-1} 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 to 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 23.9 wt.% gas for a pyrolysis temperature of 950 °C (Williams et al 1998). For such large batch reactors, there is a major drawback related to the transfer of heat to the large volume of tyres contained within the reactor. For example, the reported 950 °C pyrolysis temperature represented the maximum attained temperature over an 8 h 40 minute heating period. The reactor design would produce pyrolysis at the outer edge of the reactor and for tyres located in the inner part of the reactor and pyrolysed later in the heating cycle, the evolved gases would be subject to significant secondary cracking reactions resulting in oil decomposition and cracking to produce increased gas For example, Williams and Taylor

(1993) examined the influence of tyre pyrolysis gas residence time at high temperature by passing pyrolysis gases produced at 450 °C through a secondary reactor at temperatures from 500 to 720 °C and a gas residence time of ~30. The gas and oil yields showed a marked change with secondary reactor temperature; the gas yield increased from 10 to 20 wt.% and the oil yield decreases from 51.5 to 41.5 wt.% as the secondary reactor temperature was increased from 500 to 720°C.

2.2 Screw kiln and rotary kiln reactors

Continuous operating reactors have been developed for the pyrolysis if waste tyres. For example, Aylón et al. (2008, 2010) used a moving bed reactor and investigated the influence of various parameters, including pyrolysis temperature, between 600 °C and 800 °C and mass flow rate of tyres through the reactor on product yield and composition. The reactor was a continuous screw kiln reactor, externally heated by electrical furnaces. The reactor was fed by a screw feeder from the hopper containing shredded tyres with throughputs from 3.5 to 8.0 kg h^{-1}. Pyrolysis oils were condensed in a shell-and-tube condenser and non-condensable gases were combusted. The solid char was recovered at the end of the screw kiln reactor outlet. The reported maximum oil yield of 48.4 wt.% was obtained at a pyrolysis temperature of 600 °C and a tyre mass flow rate of 8 kg h^{-1}. The research group report that experiments on a small scale fixed bed reactor produced oil yields of 56.4 wt%, the difference compared to the moving bed screw reactor were attributed to the differences in heating rate and gas residence times between the two reactors (Aylón et al. 2008). Diez et al. (2005) also used a screw kiln reactor, externally heated by an electrical furnace to investigate the pyrolysis of shredded tyre at a pyrolysis temperature of 500/600 °C.

The plant was designed to produce gas and very little oil, so had a long gas residence time and fast heating rate. The reported product yields were ~33.5 wt.% char and ~66.5 wt.% gas.

Galvagno et al. (2002) (Reactor details in, Fortuna et al. (1997)) used a pilot scale rotary kiln reactor to investigate the influence of temperature on the product yield from pyrolysis of waste tyres. The rotary reactor was 0.4 m diameter and rotated at 3 r.p.m. and externally heated by electrical furnaces with a throughput of 4.8 kg h^{-1}. A condensation system allowed condensed fractions of heavy and light pyrolysis oil and the non-condensable gases were scrubbed to remove acid gases and then combusted in a flare. The solid residue of pyrolysis (char) was continuously discharged in a water cooled tank. A maximum yield of product oil of 38.12 wt.% was obtained at 550 °C and maximum gas yield of 10.75 wt.% at 680 °C. Li et al. (2004) also used a rotary kiln reactor to investigate tyre pyrolysis at different pyrolysis temperatures. The rotary kiln consisted of a 0.3 m diameter, 3 m long reactor rotating at between 0.45 and 0.9 r.p.m., externally heated by electrical furnaces corresponding to an effective heated length of 1.8 m. The highest oil yield of 45.1 wt.% was obtained at 500 °C pyrolysis temperature with a gas yield of 13.6 wt.%. Maximum gas yield was 18.3 wt.% at 650 °C due to the secondary cracking reactions of the oil vapour at higher temperatures and the long residence time of gases in the hot zone of the rotary kiln reactor.

2.3 Fluidised bed reactors

Fluidised bed pyrolysis of tyres has been extensively researched by Kaminsky and co-workers (Kaminsky and Sinn, 1980; Kaminsky, 1985; Kaminsky and Meenerich, 2001; Kaminsky et al., 2004; Kaminsky et al., 2009). Fluidised bed reactors have been investigated at laboratory scale with 1 kg h^{-1} throughput, technical scale with 30 kg h^{-1} throughput to pilot scale with 200 kg h^{-1} throughput. Large scale pilot plant studies were able to process whole

tyres. The fluidised bed is heated indirectly to typical temperatures of between 500 and 780 °C via radiant heat tubes within the bed of quartz sand, in which the product pyrolysis gas is combusted to provide heat. The fluidising gas is also the product gas and is preheated to 400 °C. Any ash build up in the fluidised bed is removed by a screw extractor. The product gases pass through a cyclone to remove particulate material and the oils condensed and distilled to produce two oil fractions, heavy and light oils. The gases undergo further removal of oil droplets in an electrostatic precipitator before storage. Kaminsky et al. (2009) reported that for the laboratory scale 1 kg h^{-1} fluidised bed reactor oil yields at 740 °C pyrolysis temperature were 30.2 wt% and for the 200 kg h^{-1} pilot scale reactor processing whole tyres at 700 °C, oil yield was 26.8 wt%, but on a steel free basis was similar to the laboratory reactor oil yield at 30.9 wt.%.

A laboratory scale fluidised bed reactor was used by Williams and Brindle (2003a) to pyrolyse tyre crumb (size 1.0-1.4 mm) over the temperature range of 450 to 600 °C. The reactor was 7.5 cm diameter and 100 cm high with quartz sand as the reactor bed and a throughput of ~220 g h^{-1} of tyre. The incoming fluidising air was nitrogen and was pre-heated to 400 °C by an external electrical furnace. Condensation was via a series of water cooled and dry ice/acetone cooled condensers. The maximum oil yield of 55 wt.% was found at 450 °C pyrolysis temperature which was reduced to 43.5 wt.% at 600 °C, with a consequent increase in gas yield from 2.5 wt.% to 14.0 wt.%.

A laboratory scale circulating fluidised bed reactor was developed by Dai et al. (2001) to investigate the influence of tyre particle size (0.32 mm and 0.8 mm), temperature of pyrolysis (360-810 °C) and gas residence time (1-5 s) on product yield and composition. The circulating fluidised bed was 10 cm diameter and 290 cm high. The tyre was fed to the bed via a screw feeder and quartz sand is circulated at high fluidising velocity through the reactor. Sand and char escaping the bed are trapped in two cyclones and recirculated back to the

reactor bed. Oils are condensed in a water cooled condenser and product pyrolysis gases are preheated and used as the fluidising gas. Dai et al. (2001) report a maximum oil yield of ~52 wt.% at 450 °C which decreased markedly to 30 wt% at 810 °C with a consequent increase in gas yield from ~15 wt.% to ~40 wt.%. The influence of particle size was reported as higher yields of oil (~50 wt.%) for the smaller (0.32 mm) particles compared to the larger particles of tyre (0.8 mm) which produced an oil yield of 41 wt.% at the same pyrolysis temperature of 500 °C. Longer residence times of the pyrolysis gases in the hot zone of the circulating fluidised bed reduced the oil yield from ~51 wt.% at 1 s residence time to ~48 wt.% at 5 s residence time for a pyrolysis temperature of 500 °C.

2.4 Other types of reactor

Other novel designs of pyrolysis reactors have been investigated for pyrolysis of tyres, including, spouted beds (Olazar et al., 2008; Lopez et al. 2010), vacuum pyrolysis (Roy et al., 1999), drop tube (Zabaniotou and Stavropoulos, 2003) and wire mesh and other rapid heating reactors (Leung et al., 2002, Huang and Tang, 2009). Olazar and co-workers (2004; 2008: and Lopez et al., 2010) used a conical spouted bed reactor to study the pyrolysis of tyres. The spouted bed is a type of fluidised bed reactor with the advantages of isothermal operation, high heat transfer rate, reduced gas residence time which minimises secondary reactions and better interaction of sand and solid. There is vigorous bed movement which minimises agglomeration. Olazar et al. (2008) reported an oil yield of ~62 wt.%, char yield of ~35 wt.% and gas yield of ~ 3 wt.% for the pyrolysis of waste tyre particles. In the same work they investigated the use of catalysts to determine the influence on gas and oil composition. They also used the spouted bed reactor under vacuum pyrolysis conditions

(Lopez et al., 2010). The influence of the vacuum producing oils with a higher diesel fraction and increased yield of isoprene.

Vacuum pyrolysis of waste tyres has been extensively investigated by Roy and co-workers (Roy et al., 1990; Benallal et al, 1995; Roy et al., 1999; Pakdel et al, 2001. Oil yields of up to 56.5 wt.% (Pakdel et al., 2001) from waste tyre granules have been obtained using their continuous or semi-continuous pilot scale vacuum pyrolysis system. Vacuum pyrolysis is reported to be characterised by short residence times of the pyrolysis gases as the vacuum conditions quickly remove the gases from the hot zone of the reactor, thereby minimising secondary char forming and cracking reactions (Roy et al., 1999). In addition, the influence of vacuum conditions enhances diffusion of the volatile products formed within the tyre due to the pressure gradient inside and outside the particle; the faster diffusion of the volatile gases reduces the time for secondary reactions (Lopez et al, 2010). Kinetic analysis of waste tyres using a thermogravimetric analyser showed that the thermal degradation of tyre occurred at lower temperature and was faster under vacuum conditions compared to atmospheric pressure (Lopez et al., 2009). Zhang et al. (2008) used a batch vacuum pyrolysis reactor to pyrolyse tyre granules and reported that pyrolysis oil yield increased gradually to a maximum of 48.8 wt.% at 600 °C as the pyrolysis temperature was raised from 450 to 600 °C. The oil yield is lower than that obtained by other vacuum pyrolysis reactors (Roy et al., 1999; Pakdel et al., 2001) but with higher gas yield at 16.3 wt.% gas at 600 °C.

A drop tube pyrolysis reactor was investigated by Conesa et al. (2004) to study the pyrolysis of waste tyre particles (4 mm size). The tyre particles were fed in 5 g batches into a hot (450, 750 or 1000 °C reactor temperature) reactor of 65.4 cm height. A solid CO_2 cooled condenser trapped the oils. Increasing pyrolysis temperature showed a marked reduction in oil yield from 37.8 wt.% at 450 °C, decreasing to 10.9 wt.% at 750 °C and to less than 0.01

wt.% at 1000 °C. The solid char residue yield was similar at each temperature (~37 wt.%) resulting in a high conversion of the tyre to gas of about 63 wt.% at 1000 °C.

High heating rate tyre pyrolysis using a electrically heated wire mesh microreactor system was investigated by Zabaniotou and Stavropoulos (2003). The wire mesh process involved placing about 200 mg of the tyre rubber (0.18 – 1.0 mm particle size) on a wire mesh. An electric current is passed through the mesh which rapidly raised the temperature (70-90 °C s^{-1}) of the mesh to temperatures of between 390 to 890 °C. With such rapid heating of small particles, there was a low oil yield of less than about 5 wt.% and a high gas yield which increased from ~22 wt.% at 450 °C to ~73 wt% at 860 °C.

Huang and Tang (2009) investigated high heating rates and very high temperatures to determine the conversion of tyre to gas using a plasma reactor. Maximum temperatures investigated were 1500 °C with tyre particles of 200 – 600 µm. The tyre particles are passed through the plasma reactor at feed rate of 0.2-0.5 g min^{-1} via a nitrogen gas flow. The reported highest conversion of the tyre to gas was 78.4 wt.% at 1500 °C, the gas consisting of mainly H_2 and CO.

2.5 Influence of tyre type and composition

The large majority of the research undertaken on waste tyres has used tyres from reprocessing plants where the tyres will be a mixture of different brands and types. It has also been reported (Evans and Evans, 2006) that a typical tyre could contain up to 30 different types of synthetic rubber, 8 different natural rubbers, in addition to a range of different carbon black fillers and up to 40 different additive chemicals. Kyari et al. (2005) investigated the pyrolysis of seven different types and brands of waste tyres from different source countries. They reported that the yields of oil, gas, and char were not significantly

influenced by the type and origin of the tyre. However, there were noticeable differences in the composition of the derived gases and oils. Detailed analysis of the pyrolysis oils showed variations in the concentration of certain aromatic compounds depending on the tyre type and origin. In addition, they carried out pyrolysis of a mixture of the seven tyres, and the results of both yield and composition showed that the resultant products was an average of the individual tyre yields and compositions. Cypres and Bettens (1989) also pyrolysed different types of waste tyre in a two-stage reactor, with pyrolysis in the first stage and post-pyrolysis cracking of the gases in a second reactor at higher temperatures. They showed small but significant differences in product yield depending on the six types of tyre used.

Although tyres may be composed of many different types of synthetic and natural rubber, the main rubber types used are, typically, styrene-butadiene-rubber, natural rubber (polyisoprene) and polybutadiene rubber (Williams and Besler, 1995; Seidelt et al, 2006). Williams and Besler (1995) used thermogravimetric analysis to investigate the thermal decomposition of three samples of tyre of known rubber composition and the three major rubber components of the tyres, styrene-butadiene-rubber, natural rubber and polybutadiene rubber. The thermograms showed two distinct areas of weight loss, with styrene-butadiene rubber decomposing at higher temperature and natural rubber at lower temperature, the polybutadiene rubber decomposed mainly at higher temperature but also showed initial decomposition at lower temperature. Analysis of the tyre rubbers with known rubber composition could be related to the composition of the component rubbers. The char yields from the three rubbers showed ~4wt.% of char, suggesting that the char from the pyrolysis of tyres is mainly originated from the carbon black filler. Seidelt et al. (2006) also examined the thermal decomposition of styrene-butadiene-rubber, natural rubber and polybutadiene rubber using coupled thermogravimetric analysis-mass spectrometry. They confirmed the relationship between tyre rubber composition and the temperatures of the thermal degradation

of the three component rubbers. They also reported that the main degradation product from natural rubber was xylene and isoprene dimer and from styrene-butadiene-rubber the main components were ethylbenzene, styrene and cumene.

However, of more significance in determining the product yield and composition of the oils and gases in particular is largely determined by the type of reactor used and the consequent heating rate and pyrolysis temperature, rather than differences in individual tyre compositions.

3. Tyre pyrolysis oil composition

Tyre pyrolysis oil is a dark brown/black coloured, medium viscosity oil with a sulphurous/aromatic odour. It is chemically very complex containing more than 100 identified compounds. Table 3 lists some of the reported compounds identified in tyre pyrolysis oils (Williams and Bottrill, 1995; Cunliffe and Williams, 1998a; Dai et al., 2001; Li et al., 2004; Conesa et al., 2004; Laresgoiti et al., 2004; Olazar et al., 2008; Kaminsky et al., 2009; Banar et al., 2012).

The oils have been fractionated into broad chemical class fractions and shown to be composed of aliphatic, aromatic, hetero-atom and polar fractions. Dai et al. (2001) reported a tyre oil composition from the pyrolysis of tyres in a circulating fluidised bed of 26.77 wt.% of alkanes, 42.09 wt.% aromatics, 26.64 wt.% of non-hydrocarbons and 4.05 wt.% as asphalt. Conesa et al., (1996) reported a 39.5 wt.% aliphatic fraction, 19.1 wt.% aromatic fraction, 21.3 wt.% hetero-atom fraction and 20.1 wt.% polar fraction for oils produced from a laboratory scale fluidised bed reactor at 700 °C. Aylón et al., (2008) using a screw kiln reactor to pyrolyse tyres at 600 °C reported an alkane fraction of 6.7 wt.%, aromatic fraction of 65.6 wt.% and polar fraction of 27.8 wt.%. Laresgoiti et al. (2004) reported an increase in

aromatic content of tyre pyrolysis oils from a fixed bed reactor from 53.4 wt.% to 74.8 wt.% as the temperature was raised from 300 to 700 °C.

3.1 Aromatic compounds

The main aromatic compounds found in the oil are benzene, toluene, xylenes (dimethylbenzenes), styrene, limonene and indene and their alkylated homologues. In addition, the oils contain polycyclic aromatic hydrocarbons from two-ring naphthalene to 5 ring benzopyrenes. The main aliphatic compounds are alkanes, with straight chain hydrocarbons from C_6- C_{37} and lower concentrations of alkenes.

Cunliffe and Williams (1998a) reported chemical class fractions of tyre oils produced from a fixed bed reactor at temperatures between 450 and 600 °C and showed a clear increase in the aromatic fraction and decrease in the aliphatic fraction of the oils as the temperature of pyrolysis was increased. For example, the oil produced at 450 °C consisted of the chemical fractions 51.3 wt.% aliphatic, 36.7 wt.% aromatic, 6.6 wt.% hetero-atom and 8.6 wt.% polar. However, at 600 °C pyrolysis temperature, the oil composition was 36.1 wt.% aliphatic, 45.6 wt.% aromatic, 11.6 wt.% hetero-atom and 6.6 wt.% polar fractions. Secondary reactions of the pyrolysis gases at extended residence time in the hot zone of the pyrolysis reactor will also result in increased aromatic content of the tyre oil (Cypres and Bettens, 1989; Williams and Taylor, 1993). Differences in the relative concentrations of the different fractions reported by different authors could be related to the analytical fractionation method in addition to differences in reactor characteristics, heating rate of the tyre, pyrolysis temperature, extent of secondary reactions etc.

Kaminsky et al. (2009) have reported detailed analyses of tyre pyrolysis oils obtained from pyrolysis of tyres in fluidised beds ranging in throughputs from laboratory scale at 1 kg$^-$^{1} to pilot scale at 200 kg h^{-1}. They report benzene and toluene concentrations of 4.2 wt% and

3.8 wt.% respectively for a laboratory scale reactor at 740 °C. Cunliffe and Williams (1998a) reported maximum concentrations of volatile aromatic compounds of toluene at 1.77 wt.%, total xylenes at 1.68 wt.%, styrene at 0.36 wt.%, limonene at 3.13 wt.% and indene at 0.32 wt.%. Using a rotary kiln reactor, Li et al. (2004) reported concentrations of benzene, xylene, toluene, styrene and limonene at 550 °C pyrolysis temperature of 1.49 wt.%, 2.05 wt.%, 5.16 wt.%, 1.42 wt.% and 0.42 wt.% respectively. It was reported that there was a marked influence of temperature on volatile aromatic concentrations, for example, benzene increasing from 0.40 wt.% at 450 °C to 2.09 wt.% at 650 °C, similarly toluene increased from 2.27 wt.% to 7.06 wt.% over the same temperature range. There was a corresponding decrease in limonene concentration with increasing temperature. It has been suggested that limonene decomposes to a range of products including benzene, xylene, toluene, trimethylbenzene, styrene and methylstyrene which occurs at pyrolysis temperatures above 500°C and/or with long hot zone residence times (Pakdel et al., 1992; Williams et al., 1995; Li et al., 2004).

3.2 Polycyclic aromatic hydrocarbons

Tyre pyrolysis oils contain a wide range of polycyclic aromatic hydrocarbons (PAH), but the highest concentration of PAH identified consist largely of alkylated naphthalenes, fluorenes and phenanthrenes. Table 3 shows some of the PAH identified in tyre pyrolysis oil (Williams and Bottrill, 1995; Cunliffe and Williams, 1998a; Dai et al., 2001; Li et al., 2004; Conesa et al., 2004; Laresgoiti et al., 2004; Olazar et al., 2008; Kaminsky et al., 2009; Banar et al., 2012). Concentrations of total PAH in tyre pyrolysis oils are reported at 1.72 wt% for a fixed bed reactor at 500 °C (Cunliffe and Williams, 1998a), however, higher concentrations of PAH totalling over 16 wt.% have been reported for the rotary kiln pyrolysis of waste tyres at the same temperature (Li et al., 2004). A wide range of PAH have been reported by

Laresgoiti et al. (2004), consisting of mainly naphthalene, fluorene and phenathrene and their alkylated homologues.

It has been shown that higher temperatures of pyrolysis and long residence times produce increased concentrations of PAH (Williams and Taylor, 1993; Cunliffe and Williams, 1998a). For example, for fixed bed pyrolysis of waste tyres, total PAH content of the derived oils increased from 1.53 wt.% at 450°C to 3.43 wt.% at 600°C, with alkylated compounds of naphthalene, fluorene and phenanthrene increased with pyrolysis temperature (Cunliffe and Williams, 1998a). For example, total alkylated naphthalenes increased from 0.54 wt.% to 1.43 wt.%, alkylated fluorenes increased from 0.08 wt.% to 0.26 wt.% and the alkylated phenanthrenes increased in concentration from 0.54 wt.% to 0.81 wt.% as the pyrolysis temperature was increased. Li et al. (2004) reported a similar influence of temperature but at higher concentrations of PAH, with naphthalene homologues increasing from 8.6 to 10.1 wt.%, fluorene homologues increasing from 1.17 to 2.57 wt.% and phenanthrene homologues increasing from 2.15 to 6.51 wt.% with increased pyrolysis temperature from 450 to 650 °C. Laresgoiti et al. (2004) also reported increased PAH with increased pyrolysis temperature.

Secondary cracking of tyre pyrolysis gases to produce PAH has been confirmed by experiments using secondary reactors at high temperature and long residence times. For example, Williams and Taylor (1993) for the pyrolysis of tyres in a batch reactor with post-pyrolysis heating of the tyre vapours. They found that the total PAH content of tyre derived oils increased from 1.4 wt.% at 500°C post-pyrolysis temperature to over 10 wt.% total oil at 720°C post-pyrolysis temperature. Cypres and Bettens (1989), also using a post-pyrolysis secondary reactor, found a similar trend of increasing PAH in derived tyre pyrolysis oils with secondary reactions of the gases. A Diels–Alder reaction mechanism has been suggested as being responsible for the increase in aromatic content with temperature (Cypres and Bettens,

1989; Williams and Taylor, 1993). Banar et al. (2012) used a fixed bed reactor and reported that PAH concentrations in the product oil were increased with increasing reactor heating rate. Kyari et al. (2005) analysed the tyre pyrolysis oil from different types and brands of waste tyre using a fixed bed reactor and reported different tyres produced different concentrations of single ring and PAH in the product oils.

The presence of sulphur containing PAH (PASH) and nitrogen containing PAH (PANH) have been reported. For example, Kaminsky et al (2009) reported the presence of PASH in the form of thiophene, methylthiophene, dimethylthiophene and dimethylbenzothiophene at concentration levels of about 0.1 - 0.3 wt.% for the fluidised bed pyrolysis of tyres. They also reported the presence of PANH in the form of aniline, and benzothiazol and dimethylquinoline at concentrations of ~0.1 wt.%. Williams and Bottrill (1995) undertook detailed analysis of the sulphur polycyclic aromatic compounds found in tyre pyrolysis oils. The PASH were mainly benzothiophene and dibenzothiophene and their alkylated derivatives, and naphthothiophenes and their methyl derivatives. The PASH in oils derived from the fluidised bed pyrolysis of tyres showed an increase in concentration as the temperature of pyrolysis was increased.

There has been very limited work in relation to determination of the concentration of dioxins (polychlorinated dibenzodioxins, PCDD) and furans (polychlorinated dibenzofurans, PCDF) in tyre pyrolysis oil. However, Banar et al. (2012) analysed tyre pyrolysis oil produced from a fixed bed reactor and reported concentrations of 1234678-HpCDF at 0.021 pg g^{-1}, 1234789-HpCDF at 0.015 pg g^{-1}, 123478-HxCDD at 0.008 pg g^{-1} and OCDD at 0.021 pg g^{-1}. They also reported very low concentrations of metals in the tyre pyrolysis oil, with levels of arsenic, cadmium, chromium and lead at the parts per billion level and also chloride at the parts per million level.

3.3 Fuel properties of tyre pyrolysis oils

Table 4 shows the fuel properties of tyre pyrolysis oil from several reported reports and table 5 shows the properties of petroleum derived fuel oils for comparison. Aydin and Ilkilic (2012) investigated the sulphur content of tyre pyrolysis oil in relation to temperature and found that differences of about 0.3 wt% lower sulphur content could be found for an oil produced at 550 °C compared to a tyre pyrolysis oil produced at 400 °C. They also found that increasing the pyrolysis temperature increased the sulphur content of the derived pyrolysis oil. Cunliffe and Williams (1998a) also found that lower pyrolysis temperatures of 450 °C and 475 °C produced a higher sulphur content (1.4 wt.%) compared to oils produced at higher temperatures.

The fuel properties of a liquid fuel define the characteristics of the fuel in terms of its potential performance in a combustion system, storage and transport issues, likely emissions, distillation range etc. The flash point of a liquid fuel represents the temperature that flammable gases are produced and will ignite and indicates the fire hazards associated with storage, transport and use of the fuel. The flash point of the tyre-derived oils is generally low when compared to petroleum refined fuels due to the tyre oil being an unrefined oil with a range of boiling point fractions, including volatile hydrocarbons. The carbon residue test is a measure of the tendency of the oil to form carbon under poor combustion conditions which may lead to carbon coking of diesel engine fuel injector nozzles or spray combustion burners. The tyre oil carbon residues are quite high at between 1.78 - 2.2% compared to gas oil at <3.5%, suggesting that nozzle or spray burner blockage with extensive time of use may be an issue. The viscosity of a fuel influences the flow of the fuel through pipework, valves and

pumps and also fuel atomization in engines and spray burners. The viscosity of the tyre oils was similar to that of gas oil. The sulphur content of the tyre pyrolysis oils are between 0.11 to 1.54 wt.%. The sulphur content is similar to that of a light fuel oil.

Aydin and Ilkilic (2012) investigated the reduction of sulphur in tyre pyrolysis oils. They determined a range of fuel properties of the oil derived from the pyrolysis of waste tyres using a calcium hydroxide additive, used to reduce the sulphur of the tyre pyrolysis oil. They found that the product pyrolysis oil had fuel properties similar to petroleum derived diesel fuel. Blended mixtures of the modified tyre pyrolysis oil and diesel fuel showed fuel properties which were very similar to diesel. The boiling point/distillation range of the tyre pyrolysis oils reflected the fact that the oil was unrefined and consequently would have a wide range of boiling points for the components of the oil. The caloric value of the tyre oils ranged between 38 to 42.66 MJ kg $^{-1}$ and was comparable with that of the petroleum fuels shown in Table 5. Others have reported the calorific value of the tyre pyrolysis oil to be between 38 and 49.5 MJ^{-1} (Williams et al, 1998; Li et al., 2004; Murugan et al, 2008a; Banar et al, 2012; Rada et al, 2012). Kar (2011) used expanded perlite as a catalyst mixed with waste tyre in an attempt to improve the fuel properties of the product pyrolysis oil. Perlite is a natural glassy volcanic rock composed mainly of silica and alumina which is heated to between 850 – 1000 ℃ to produce a porous catalyst support. The support was used with added metals to produce the catalytic activity. Without the catalyst the oil yield was 60.0 wt.% and with the catalytic pyrolysis, oil yield was improved to 65.1 wt.% with a perlite:waste tyre ratio of 0.10. The fuel properties of the product oil were reported and were shown to be similar to conventional petroleum fuels in terms of H/C ratio, density, viscosity, calorific value and elemental composition. The author suggesting that the product pyrolysis-catalysis oil could be successfully blended with various conventional fuels.

A further test related to the fuel properties of an oil is the burning rate coefficient determined using a single droplet combustion test. Since combustion in diesel engines and furnace and boiler burners involves spraying the liquid fuel under pressure through a nozzle to form fine droplets which are then combusted. The test involves combustion of single droplets of fuel of different diameters and the rate reflects the reduction in the diameter of the droplet as it combusts. Williams et al. (1998) reported a burning rate coefficient for tyre pyrolysis oils of 0.75 mm s^{-1} which compares with the coefficients for gas oil of 0.88 mm s^{-1} and for light fuel oil of 0.82 mm s^{-1}.

3.4 Combustion of tyre pyrolysis oils

Murugan et al. (2008a, 2008b, 2008c, 2008d) have extensively investigated the use of tyre pyrolysis oil blended with petroleum diesel fuel in a direct injection diesel engine. For blended tyre pyrolysis oil-diesel fuel blends, Murugan et al (2008a) reported that the brake thermal efficiency (overall efficiency) of the engine was only marginally influenced by the use of the tyre pyrolysis oil-diesel fuel blends compared to using diesel fuel alone at blends of 10%, 30% and 50% of tyre pyrolysis oil. In some cases, there was a marginal increase in brake thermal efficiency with the blended fuel. They also reported that there was no seizing of the engine or injector nozzle blocking with the use of the blended tyre oil and diesel fuel. In terms of emissions, it was reported that hydrocarbon emissions were significantly increased by 15% and 21% when tyre oil-diesel fuel blends of 30% and 50% respectively were used under peak load conditions compared to diesel fuel. This was attributed to the higher concentration of PAH in tyre oil compared to diesel fuel. In addition, nitrogen oxides (NOx) emissions were found to be 4.5% and 10% higher for the 30% and 50% tyre oil blends respectively compared to diesel fuel under peak load conditions. The emission of smoke

(particulate material) was increased by 7% compared to diesel fuel when the 50% blend of tyre oil and diesel was used at peak load.

Higher ratios of tyre pyrolysis oil-diesel fuel with up to 90% addition to diesel fuel were also investigated by Murugan et al. (2008b, 2008d). At higher blend ratios the tyre oil was modified by sulphur reduction, moisture removal and distillation prior to blending. It was reported that the direct injection diesel engine could not operate satisfactorily on 100% modified tyre pyrolysis oil, but could at 90% tyre oil with 10% diesel fuel. A small (2%) reduction in engine efficiency and an 11% increase in hydrocarbon emissions was observed but an 18% decrease in NOx was reported at peak load using the 90% tyre oil blend. There was however a marked increase in the emission of smoke.

Williams et al. (1998) investigated the combustion of raw tyre pyrolysis oil compared to petroleum derived gas oil in a 1.6 m long by 0.5 m diameter ceramically lined furnace. The liquid fuel spray burner used a pressurised spray atomiser of 0.4 mm diameter with an in-line particulate filter upstream of the burner. The authors reported that the furnace was able to operate successfully for several hours without problem, producing no particulate or PAH emissions at the normal operating conditions of the furnace at 6% excess oxygen combustion conditions. Combustion of tyre pyrolysis oil produced flue gas SO_2 concentrations of 530 ppm at 2.1% excess oxygen and 440 ppm at 7.6% excess oxygen, compared to 40 ppm and 55 ppm respectively for the gas oil fuel. NOx emissions were 374 ppm at 2.1% excess oxygen and 343 ppm at 7.6% excess oxygen approximately three times higher than were found for the combustion of gas oil. The results for SO_2 and NOx emissions were consistent with higher fuel sulphur (1.45 wt.%) and nitrogen (0.45 wt.%) contents in the tyre oil compared to the gas oil (0.2 and 0.45 wt.% respectively).

4. Char characteristics

Table 2 showed that the char produced from the pyrolysis of tyres ranges from 22-49 wt.%, with a typical values around 38-40 wt.%. For example Kyari et al (2005) reported that the char yield from the fixed bed pyrolysis of seven different types and brands of tyre obtained from a range of locations were between 37.1 and 41.7 wt.%. They also reported that the surface area of the chars ranged from 64.5 m^2 g^{-1} to 83.8 m^2 g^{-1} depending on the tyre and brand of tyre, and consequently the rubber formulation of the tyres. Table 6 shows a range of reported properties of chars derived from the pyrolysis of tyres. The chars have high carbon contents of up to 90 wt.% and high sulphur contents reported to be between 1.9 and 2.7 wt.%. However, most notably the chars have a high ash content reported at between 8.27 and 15.33 wt.% related to the additive metals, mostly zinc, added in the formulation of the tyre and dirt material found with the waste tyres.

The influence of process conditions on the characteristics of product chars have been investigated by several researchers. For example, Cunliffe and Williams (1998b) reported char characteristics in relation to pyrolysis temperature over the range of 450 to 600 °C for 1.5 kg batches of tyre using a fixed bed reactor. They reported that the volatile content and hydrogen content of the product chars was reduced with a small increase in surface area and mesopore volume as the temperature of pyrolysis was increased. This was attributed to the loss of high molecular weight solid hydrocarbons with increasing temperature which resulted in pore widening and consequent increase in surface area. There was little influence of pyrolysis temperature on the trace metal or sulphur content of the chars over the temperature range investigated. Li et al. (2004) also investigated the characteristics of chars produced from a rotary kiln reactor over a similar temperature range of 450 to 650 °C. They also reported that the volatile content of the product chars decreased with increasing temperature,

from 16.61 wt.% to 6.27 wt.%, with typical surface area ~89 m^2 g^{-1}. Galvagano et al. (2002) also used a rotary kiln reactor and reported a decrease in volatile content from 12.78 wt.% to 5.24 wt.% with increasing pyrolysis temperature from 550 to 680 °C. The metals content of the chars was also reported, but there appeared to be no particular trend in relation to increased temperature of pyrolysis. Kaminsky and Mennerich (2001) showed that increasing the pyrolysis temperature for the fluidised bed pyrolysis of a synthetic tyre rubber produced chars which increased from 76 m^2 g^{-1} to 85 m^2 g^{-1} as the pyrolysis temperature was increased from 500 to 600 °C. Conesa et al. (2004) investigated the influence of temperature but over a much higher temperature range of pyrolysis of between 450 °C and 1000 °C. Volatile content of chars decreased from 7.78 wt.% at 450 °C to 1.06 wt.% at 1000 °C, hydrogen also decreased (from 0.60 to 0.17 wt.%) with a corresponding increase in surface area from 93 m^2 g^{-1} to 139 m^2 g^{-1}. Metal contents in the chars were reported to be similar for the 450 °C and 750 °C chars, but at the higher temperature of 1000 °C there was significant vaporisation of the zinc out of the char into the gas phase. The zinc concentration decreased in the char from 6.68 wt.% to 0.935 wt.% as the temperature was increased from 450 to 1000 °C.

There have been many studies investigating the properties of the char as a substitute carbon black (Darmstadt et al, 1995; Sahouli et al., 1996; Roy et al., 1999; Kaminsky and Mennerich, 2001; Pantea et al, 2003; Tang and Huang, 2005; Mikulova et al., 2013). The carbon black/char produced from pyrolysis of tyres differs from commercial carbon black in that the char consists of the recovered carbon black and also pyrolytic char. Williams and Besler (1995) have shown that the main source of the carbonaceous char is the original carbon black filler, since the main rubber components of the tyre such as styrene-butadiene rubber, natural rubber and polybutadiene rubber only produce about ~4 wt.% of char.

Darmstadt et al. (1995) reported that carbon blacks obtained from the pyrolysis of tyres in a vacuum pyrolysis reactor at 500 °C contained less pyrolyitic carbon compared to

pyrolysis under atmospheric pressure conditions. The pyrolytic carbon deposits on the original carbon black deactivating the carbon black activated sites making the carbon less effective in relation to the original carbon black added to the tyre. In addition, Darmstadt et al. (1995) and Sahouli et al. (1996) show that the surface chemistry of the recovered carbon black is similar to low grade commercial carbons. The surface roughness of the carbon black is an important property in that it influences the interaction of the active sites of the carbon black with the elastomer. The authors report that increasing pyrolysis pressure and to some extent temperature in vacuum pyrolysis reduces the surface roughness. Kaminsky and Mennerich (2001) also noted the presence of pyrolytic carbon on the recovered carbon black (char) from the fluidised bed pyrolysis of synthetic tyre rubber at 600 °C and showed that the surface area of the recovered char was 85 m^2 g^{-1} compared to the carbon black used in the tyre rubber formulation of 115 m^2 g^{-1}. They also noted that the high ash content of the char (~10wt.%) would represent a problem for the use of the char as a commercial carbon black. A typical carbon black used in tyre manufacture must be below 0.5 wt.%. (Tang and Huang, 2005). Cunliffe and Williams (1998b) also highlighted the high ash content of the recovered char as a drawback to its use as a substitute carbon black, with ash contents reported at around 12 wt.%. They used an acid wash process on the chars that could reduce the ash content by up to 90%. A typical carbon black used in tyre manufacture must have an ash content below 0.5 wt.%. (Tang and Huang, 2005). Tang and Huang (2005) used rapid heating, plasma pyrolysis of tyre particles to produce a char product and comparison was made with commercial carbon blacks. The surface area of the chars was 64.8 m^2 g^{-1} compared to a commercial carbon black (N330) at 80 m^2 g^{-1}. In addition, the ash content was 15.14 wt.% compared to the commercial carbon black at 0.4 wt.%.

5. Gas composition from the pyrolysis of waste tyres

Table 7 shows the analysis of the gases produced from the pyrolysis of waste tyres. The main gas components are hydrogen (H_2), methane (CH_4), ethane (C_2H_6), ethene (C_2H_4), propane (C_3H_8), propene (C_3H_6), butane (C_4H_{10}), butene (C_4H_8), butadiene (C_4H_6), carbon dioxide (CO_2), carbon monoxide (CO) and hydrogen sulphide (H_2S). The gas composition arising from the tyres is dependent on the composition of the various rubbers used in tyre manufacture, such as styrene–butadiene–rubber, natural rubber (polyisoprene), nitrile rubber, chloroprene rubber, polybutadiene rubber. The thermal degradation process will produce highly reactive free radicals which are often sub-units of the original rubber molecule (Dodds et al., 1983). As the tyre rubbers are thermally degraded during the pyrolysis process, the main primary degradation products produce high concentrations of alkenes and dienes and butadiene in particular. Secondary reactions of the product pyrolysis gases in the hot zone of the reactor will also lead to the formation of light hydrocarbons from the oil vapours produced during pyrolysis. The gas has a significant calorific value and has been reported to be between 20 MJ m^{-3} to more than 65 MJ m^{-3} depending on the gas composition which in turn would depend on the temperature of pyrolysis, heating rate, type of reactor etc. (Williams et al., 1990; Leung et al., 2002; Kyari et al, 2005; Rada et al., 2012). It is suggested that the gas has sufficient energy value to provide the process fuel to heat the tyres to the required pyrolysis temperature.

Kyari et al. (2005) analysed the gases produced from the pyrolysis of different types and brands of tyre in a fixed bed batch reactor at 500 °C. The gas compositions for each type of tyre produced significantly different gas compositions, for example hydrogen yield ranging from 13.8 vol% to 27.6 vol% and methane ranging from 14.1 vol% to 27.9 vol% depending on tyre type. The calorific value of the total gases was also influenced by tyre type, ranging

from 29.9 MJ m^{-3} to 42.1 MJ m^{-3}. Cypres and Bettens (1989) also reported significant differences in gas composition from the pyrolysis of different brands of tyre. For example, for the six different tyres they investigated, there were variations of more than 100% in the reported concentrations of hydrogen, ethane and ethene.

The influence of pyrolysis temperature on product gas composition has been investigated by several researchers. Overall gas yield is known to increase with increasing pyrolysis temperature as, the higher temperature results in thermal cracking of the pyrolysis oil vapours producing higher gas yields and lower oil yields as discussed in Section 2. Increasing pyrolysis temperature produces an increase in hydrogen, methane and C_1-C_4 hydrocarbons. For example, Kaminsky et al. (2009) pyrolysed tyres in a 1.4 kg h^{-1} throughput fluidised bed and showed total gas yield increasing from 20 wt.% at 598 °C to 24 wt.% at 600 °C and to 33 wt.% at 700 °C pyrolysis temperatures. They also reported hydrogen yields increasing from 0.59 to 1.1 wt.%, methane from 2.9 to 6.9 wt.%, C_2 hydrocarbons from 2.8 to 5.8 wt.% and C_3 hydrocarbons increasing from 2.96 to 5.03 wt.% as the pyrolysis temperature was increased from 598 to 700 °C. Carbon dioxide, carbon monoxide and hydrogen sulphide also showed an increase with increasing fluidised bed pyrolysis temperature. Williams and Brindle (2003a) also for a fluidised bed reactor, but at 0.2 kg h^{-1} throughput and a temperature range of 450 to 600 °C, reported lower total gas yields ranging from 2.5 wt.% at 450 °C, 6.0 wt.% at 525 °C and 14 wt.% at 600 °C. However, increasing pyrolysis temperature showed that hydrogen and the hydrocarbons increased in yield, the main gas yields were for methane, ethene, propene and butadiene.

Galvagano et al. (2002) used a rotary kiln reactor between 550 and 680 °C and reported an increase in gas percentage composition for hydrogen, carbon monoxide, methane, ethane, ethene and C_{3+} hydrocarbons. They also reported an increase in hydrogen sulphide with increased pyrolysis temperature. Leung et al. (2002) used a fixed bed reactor, but at

temperatures from 500 °C up to 1000 °C and reported that the main gases produced were hydrogen, methane and ethene. Between 800 °C and 1000 °C, hydrogen continued to increase in yield, but methane and ethene showed a small decrease. Conesa et al. (2004) also investigated high temperature pyrolysis of tyres at 450, 750 and 1000 °C in a drop tube reactor. Methane yield showed a marked increase with increasing pyrolysis temperature, whereas carbon dioxide and ethene decreased between 750 and 1000 °C pyrolysis temperature.

6. Higher value products from waste tyre pyrolysis

Attempts have been made to increase the value of tyre pyrolysis products, through for example, selective pyrolysis temperature, post pyrolysis selective condensation, distillation of the product oil and the use of catalysts to influence the oil or gas composition or through upgrading of the char to produce activated carbon or higher value carbon black.

6.1 Chemicals from tyre pyrolysis oils.

Table 3 showed that the tyre pyrolysis oils contain a wide range of chemicals. However, of great interest the oils have been shown to contain significant concentrations of valuable chemicals such as, benzene, toluene, xylenes, styrene and limonene which are used in the chemical industry (Pakdel et al., 1992; Cunliffe and Williams 1998a; Li et al., 2004; Kaminsky et al., 2009). For example, benzene is used to produce derivatives such as ethylbenzene, cyclohexane and cumene which are used for the production of plastics, resins, fibres, surfactants, dyestuffs and pharmaceuticals (Franck and Stadelhofer, 1988). Toluene is used in the production of pesticides, dyestuffs, surfactants and solvents. Xylenes have

applications in the plastics industry to produce plasticisers, polyester resins and fibres and for use in the dyes and pigments industries. Styrene is used in the production of plastic materials and is also used to make synthetic rubber and other polymers. Limonene is used for example, in the formulation of industrial solvents, resins and adhesives and for the production of fragrances and flavourings (Pakdel et al., 1992; (Franck and Stadelhofer, 1988).

Tyre pyrolysis oils may contain high concentrations of such chemicals, depending on process conditions and type of reactor. For example, Kaminsky et al. (2009) reported a benzene yield in relation to the mass of feedstock tyre of 9.2 wt.% and toluene yield of 6.0 wt.% for the fluidised bed pyrolysis of tyre pieces in a 30 kg h^{-1} throughput reactor at 780 °C. Dai et al. (2001) used a circulating fluidised bed reactor and reported high concentrations of limonene and indene in the product oil. Kyari et al. (2005) have shown that limonene concentration varied between 2.82 wt.% and 4.76 wt.% and ethylbenzene varied from 0.74 wt.% to 1.51 wt% depending on the type or brand of tyre pyrolysed.

Laresgoti et al. (2004) pyrolysed tyres in a fixed bed autoclave reactor continuously purged with nitrogen. The composition of the derived oil was shown to be very complex, with 132 different compounds identified. The main compounds with concentrations greater than 1% were toluene, dimethylcyclohexenes, ethylbenzene, xylenes, styrene, methyloctene, ethylmethylbenzenes, methylethenylbenzenes and limonene. Concentration of toluene was 4.4%, 3.48% xylene, and 5.12% limonene at 500 °C pyrolysis temperature, the data being reported as chromatogram peak area percentage, with total percentage peak area of all the compounds identified being 75.0%. They also investigated the influence of temperature from 300 to 700 °C on oil composition and showed that limonene concentration (reported as chromatogram peak area) decreased from 21.07% at 300 °C to 3.29% at 700 °C. Benzene, ethylbenzene and xylenes also showed a decrease in concentration at high temperature. Olazar et al. (2008) reported a limonene concentration of 26.8 wt.% in the oil from the

pyrolysis of tyres in a conical spouted bed reactor. The high concentration was reported to be due to the short residence time of the primary pyrolysis products in their reactor which minimised the cracking of the limonene to aromatic and polyaromatic hydrocarbons.

However, Li et al. (2004) also investigated the influence of temperature between 450 to 650 °C on the concentration of various volatile aromatic hydrocarbons. They reported an increase in benzene from 0.40 wt.% to 2.09 wt.%, toluene from 2.26 wt.% to 7.05 wt.%, xylene from 1.53 wt.% to 2.01 wt.% and styrene from 1.20 wt.% to 2.64 wt.%. The increases in benzene, toluene, xylene and styrene were attributed to the thermal degradation of limonene, which decreased from 5.44 wt.% to 0.07 wt.% as the temperature of pyrolysis was increased from 450 to 650 °C (Pakdel et al., 1992, Cunliffe and Williams, 1998a)

Vacuum pyrolysis of tyres has shown a yield of limonene of 3.6 wt.% of feedstock tyre, but on distillation yields of 15 wt% of limonene were found in the naphtha fraction which constituted 26.8% of the total pyrolysis oil (Pakdel et al, 1992, 2001) Stanciulescu and Ikura (2006) also distilled tyre pyrolysis oil produced from an ablative reactor system and reported that vacuum distillation of the oil produced a naphtha yield of 25.5 wt% containing 16.3 wt.% limonene. They also reported a toluene concentration of 11 wt.%, xylene at 23.8 wt.%, styrene at 8 wt.% and benzene at less than 3 wt.%. Redistillation of the fraction increased the limonene concentration to approximately 32-37 wt.% (Stanciulescu and Ikura, 2006).

Williams and Brindle (2003c) examined the use of post-pyrolysis selective temperature condensation of tyre pyrolysis oils to concentrate higher value aromatic compounds. Three separate condensers were used fixed at 100, 150, 200 or 250 °C were investigated together with a final condenser held at –70 °C to trap the final condensable gases. The influence of the type of packing material within the condenser system was also examined. The results showed that the concentration of limonene in the oil fraction collected

in the first condenser at a condensation system operating temperature of 100 °C was 1.5 wt%, and was 6.8 wt% in the final condenser. At 250 °C condenser temperature the concentration of limonene in the oil in the first condenser was reduced to 0.5 wt% and was 5.6% in the final condenser. The type of packing material in the condensers was also shown to influence the concentrations of the aromatic compounds found in the condensers.

6.2 Catalytic pyrolysis of waste tyres

Catalysts have been used in the tyre pyrolysis system to increase the yield of aromatic compounds. Williams and Brindle, (2003b) investigated the use of two types of Y zeolite catalyst (CBV-400 and CBV-780) and a zeolite ZSM-5 catalyst for the production of higher value aromatic hydrocarbons in relation to the catalyst:tyre ratio. They used a fixed bed tyre pyrolysis reactor at 500 °C and the pyrolysis vapours were passed directly to a heated secondary catalysis reactor also at 500 °C. They reported a decrease in oil yield from 55.8 wt.% to ~32 wt.% as the amount of catalysts in the secondary reactor was increased and a consequent increase in gas yield, mainly methane, propane and isobutene. However, examination of the oil showed a dramatic increase in concentration of benzene, xylenes and toluene. For example, for the Y zeolite (CBV-400) produced a product oil containing 24 wt.% toluene, 5 wt.% benzene, 20 wt.% m/p-xylenes and 7 wt.% o-xylene. The Y zeolite (CBV-400) with larger pore size and higher surface activity was found to produce the higher aromatic content in the product oils. They also reported a marked increase in concentration of naphthalenes and alkylated naphthalenes as the catalyst:tyre ratio was increased. Williams and Brindle (2002) also used the same reactor system and the Y zeolite CBV-400 and ZSM-5 catalysts and investigated the influence of secondary catalyst temperature from 430 to 600 °C. For the Y-zeolite (CBV-400) catalyst, benzene increased from 2.8 to 10.2 wt% as the

catalyst bed temperature was increased from 430 to 600 °C. Toluene increased from 16.3 to 21.7 wt%. However, m/p-xylene decreased with increasing catalysts temperature above 530 °C, falling from 14 to 8.5 wt%, o-xylene also decreased from 4.8 to 2.7 wt%. The authors (Williams and Brindle 2003a) extended the research to investigate the pyrolysis-catalysis of tyres in a fluidised bed reactor. The tyre particles were pyrolysed in a 0.2 kg h^{-1} fluidised bed with a fixed catalyst bed placed in the freeboard of the reactor. Although benzene, xylene and toluene concentrations increased in the product oil in the presence of the catalysts, the concentrations were lower compared to the fixed bed reactor. The reduced concentrations of aromatic products was attributed to the shorter residence time of the product tyre pyrolysis gases passing through the fixed catalyst bed due to the increased gas velocity in a fluidised bed reactor which is required to maintain the fluidisation of the sand bed.

Olazar et al. (2008) also investigated the use of HY and HZSM-5 zeolite catalysts using a conical spouted bed reactor. They reported an increase in the concentration of single ring aromatic compounds in the oil from 20.17 wt.% in the absence of the catalysts to 32.49 wt.% with the HZSM-5 catalyst and to 40.49 wt.% with the HY catalyst. In addition, the presence of the catalyst in the pyrolysis reactor system led to increased benzene, toluene and xylene concentrations compared to only thermal pyrolysis; from 0.21 wt.% to 3.64 wt.% for benzene, 0.78 wt.% to 7.39 wt.% for toluene and from 1.23 wt.% to 9.00 wt.% for the xylenes in the presence of the ZSM-5 catalyst. For the HY catalyst, there were only small increases in benzene, xylene and toluene. They also reported that polyaromatic hydrocarbons were markedly increased with the HY catalyst but less so with the ZSM-5 catalyst. For example, naphthalene increased from 0.24 wt.% to 4.95 wt.% and the methyl-, dimethyl- and trimethyl naphthalenes increased from 0.22 to 11.9 wt.% for the HY catalyst. Shen et al (2007) also investigated the use of zeolite Y and ZSM-5 type catalysts using a two-stage (pyrolysis-catalysis) fixed bed reactor. They reported a dramatic increase in single ring aromatic

compounds when the catalysts were used. Analysis of the light fraction (<220 °C) of the oil produced after catalysis showed concentrations of toluene of 11.62 wt.%, benzene 1.6 wt.% and xylenes of 16.69 wt.% for the Y catalyst. Zhang et al. (2008) investigated the pyrolysis of tyres under vacuum conditions between 450 to 600 °C in the presence of Na_2CO_3 and NaOH in an attempt to increase the concentration of limonene in the oil and consequently in the distilled naphtha fraction. They obtained concentrations of 12.39 wt.% limonene in the naphtha distillation fraction of the tyre oil derived from vacuum pyrolysis of tyres with the NaOH additive. However, no improvement was obtained with the Na_2CO_3 additive.

6.3 Hydrogen from waste tyre pyrolysis

There is much interest in producing hydrogen from various materials, including waste tyres to help in the fulfilment of the predicted hydrogen economy of the future. For example, Mastral et al. (2002) have suggested that pyrolysis of tyres to produce an oil that is subsequently gasified with oxygen to produce hydrogen. They showed that 1 kg of waste tyre could be converted to 0.158 kg of hydrogen using oxygen gasification and the presence of steam. The hydrogen derived from the tyre hydrogen content and the steam input via the water gas shift reaction conversion of carbon monoxide. The use of post-pyrolysis catalysis at higher temperature using nickel based catalysts has been investigated to produce hydrogen from waste tyres (Elbaba et al., 2010, 2011; Elbaba and Williams, 2012). Elbaba et al. (2010) used a reactor system which consisted of fixed bed pyrolysis of tyres at 500 °C, the tyre pyrolysis gases were then passed directly to a fixed bed of a nickel based Ni-Mg-Al catalyst at 800 °C and reacted with steam. They also reported hydrogen production from several different rubbers used in tyre manufacture. The gas yield from pyrolysis-gasification increased from 22.2 wt.% in the absence of steam and catalyst to 36.2 wt.% in the presence of

steam and catalyst. The gas consisted of more than 65 vol% of hydrogen, representing conversion of tyre to hydrogen of 5.43 wt.%. It was reported that polybutadiene rubber produced 15.26 wt.% of hydrogen, styrene-butadiene-rubber produced 12.00 wt.% hydrogen and natural rubber 8.98 wt.% hydrogen during pyrolysis-catalytic steam gasification. Elbaba and Williams, 2011, 2012) further investigated the influence of various process conditions on the yield of hydrogen using the same reactor system. They showed that increased hydrogen production could be achieved at increased nickel content of the catalyst, high catalyst temperature (900 °C), higher catalyst:tyre ratio (2.0 g g^{-1}) and higher steam flow rate (10.4 g h^{-1}).

6.4. Carbon black and activated carbons from waste tyre pyrolysis

Upgrading the tyre product char has centred on improving the characteristics of the char for recovered carbon black or through post-pyrolysis activation to produce activated carbons. Post-pyrolysis heat treatment (between 670 to 860 °C) to minimise pyrolytic carbon deposition has been applied to the vacuum pyrolysis of tyres (Pantea et al., 2003). The surface chemistry of the resultant carbon blacks was changed by the secondary heat treatment producing a more polyaromatic character and the electrical conductivity of the carbons were improved to values greater than commercial carbon blacks.

The production of activated carbons from carbonaceous chars requires and activating agent such as steam or carbon dioxide. The activating agent reacts with the carbon of the char to produce mainly hydrogen, carbon monoxide, carbon dioxide and methane when steam is used and for carbon dioxide as the activating agent, carbon monoxide is the main gas product. The reaction with the carbon to produce gases opens up the pores of the char to produce higher surface areas, approaching those of activated carbons of typically between

400 and 1500 m^2 g^{-1} (Cunliffe and Williams, 1999). This results in loss of carbon or 'burn-off' of the carbon which is increased at increased gasification temperatures and/or extended reaction time. Because tyre pyrolysis chars contain typically between 8 and 15 wt.% ash (Table 6), the loss of carbon increases the relative wt.% of the ash. With typical burn-off carbon losses of between 50 and 70 wt.%, the ash content can increase to more than 30 wt.% of the product activated carbon.

Cunliffe and Williams (1998b; 1999) investigated the upgrading of tyre pyrolysis char produced from the fixed bed pyrolysis of tyres at 450 °C using a fixed bed reactor and steam or carbon dioxide as the activating agent at activation temperatures of 835 °C, 865 °C, 900 °C and 935 °C. The production of the activated carbons required removal of the ash in the product activated carbon using concentrated hydrochloric acid for 90 minutes which reduced the ash content to between 2 and 5 wt.%. The maximum surface area obtained for the product activated carbon was obtained using steam at 935 °C activation temperature and 65 wt.% carbon burn-off was 640 m^2 g^{-1}. The pore size characteristics of the carbons showed that they were mainly mesoporous carbons. The burn-off reaction sequence involved micropore formation, pore widening and at longer burn-off times, pore wall destruction and loss of surface area. Carbon dioxide activation produced activated carbons with a 20% lower surface area than those produced with steam

Teng et al. (1995) reported the pyrolysis of waste tyres in a thermogravimetric analyser at temperatures up to 900 °C and the subsequent activation of the product chars in a carbon dioxide/helium atmosphere, at 900 °C. They reported surface areas of the pyrolysis chars of typically less than 100 m^2 g^{-1}. However, after activation and with 50% burn-off, surface areas of up to 813 m^2 g^1 (980 m^2 g^{-1} on an ash free basis) were reported. Zabaniotou and Stavropoulos (2003) used a very high heating rate wire mesh reactor to produce chars from the pyrolysis of waste tyres. The product chars were then activated in a fixed bed

reactor system using either steam or carbon dioxide as the activating agent and at reaction temperatures of 850 to 1000 °C and with varying reaction times. They reported maximum surface areas of ~600 m^2 g^{-1} for both steam and carbon dioxide activating agents at the higher temperatures of reaction and at longer activation times, i.e. higher degrees of burn-off. Li et al. (2004) used a pilot scale rotary kiln reactor to pyrolyse tyres over a range of temperatures from 450 to 650 °C. The product char produced at 550 °C was subsequently activated in a fixed bed reactor using carbon dioxide and at temperatures between 850 and 950 °C for 4 hours. They reported that as the activation temperature was increased from 850 to 950 °C in the presence of the carbon dioxide, the burn-off increased from 21.3% to 51.3% with a consequent increase in surface area of the activated carbons from 125 m^2 g^{-1} to 306 m^2 g^{-1} (the maximum surface area achieved). Helleur et al. (2001) used a continuous ablative reactor system to pyrolyse waste tyres at 550 °C, the ablative system providing high heating rates and rapid removal of products. The product chars were subsequently carbonised under nitrogen at 900 °C for one hour prior to activation at 900 °C using steam or carbon dioxide and at different activation times. The maximum reported surface are of the product activated carbons was 302 m^2 g^{-1}, achieved using steam at 900 °C for 3 hours activation time

7. Commercial and semi-commercial tyre pyrolysis systems

Table 8 shows examples of commercial and semi-commercial tyre pyrolysis systems from around the world. The table shows some examples, rather than an exhaustive list of the wide range of companies which have developed tyre pyrolysis technologies. Batch tyre pyrolysis reactors have throughputs of typically 1-2 tonnes per day and for increased throughputs additional modules would be added. For larger throughputs continuous tyre pyrolysis reactors have been developed, the most common being rotary kiln reactors.

Kouei Industries (2013) have developed a batch reactor which can process one tonne batches of whole tyres in a pyrolysis cycle which with a typical two unit system can process 16 tonnes per day of waste tyres. The tyres are placed in an inner cartridge which is placed into a furnace. The furnace heats the tyres using tyre pyrolysis oil produced by the pyrolysis process. The heating time is of the order of 3 hours. The product pyrolysis gases pass to vertical condensation columns which condenses the oil into light and heavy oil fractions, while gases exit from the top of the condensers. At the end of the pyrolysis cycle the cartridge containing the char and steel is removed from the furnace and another reactor cartridge is inserted into the furnace containing a further one tonne batch of tyres. The original cartridge is left to cool and the char is removed and separated from the steel using magnetic separation and washing. No-waste Technology (2013) also produce a batch pyrolysis system to process whole waste tyres. The system also comprises an inner reactor which is placed inside a furnace. Each reactor processes approximately one tonne of tyres over a process cycle of 4-6 hours, representing 4 tonnes per day throughput. The oils are condensed to produce a fuel oil and off-gases are scrubbed and stored under pressure. The char is separated from the steel and processed via milling/grinding for sale as carbon black. From one tonne of tyres, the products are approximately 380 kg of char, 300 kg pyrolysis oil, 170 kg steel and 150 kg of gas, mainly composed of methane.

Xinxiang Doing Renewable Energy Equipment Co. Ltd., (2013) produce several sizes of continuous tyre pyrolysis systems ranging from 6 to 10 tonnes per day throughput of waste tyres. The system is based on a rotary kiln reactor of size ranging from 2.2 m to 2.8 m diameter and length from 5.5 m to 8 m depending on throughput. The rotary kiln rotates at approximately 0.4 r.p.m. The oil is condensed into heavy and light oil fractions and in some cases a catalytic chamber is also included prior to oil condensation. Oil yield is reported to be between 45 and 52 wt.%, char at 30 wt.% and steel at between 12-15 wt.%. The product gas

is cleaned and combusted and the hot flue gases are recycled to produce indirect heating of the rotary kiln reactor to provide the energy requirements for the pyrolysis process. FAB, India (2013) also produce similar rotary kiln reactors to process waste tyres. Reactor capacities range from 5 to 12 tonnes per day of waste tyres, reactors ranging from 2.2 m to 2.6 m diameter and length from 6.0 m to 6.6 m.

7. Conclusions

A review of the literature related to the pyrolysis of waste tyres has shown that most research has been carried out using a range of reactors, such as fixed-bed (batch), screw kiln, rotary kiln, vacuum and fluidised-bed. Tyre pyrolysis has also been investigated using other novel designs of reactors, for example, spouted beds, vacuum pyrolysis, drop tube reactors and wire mesh and other rapid heating reactors. The yield and composition of the products produced from pyrolysis, in particular the oils and gases, are largely determined by the type of reactor used and the temperature and heating rate. It is found that higher temperatures of pyrolysis and long gas residence times in the hot zone of the reactor can crack the oil to gas. The oil produced from pyrolysis of tyres is chemically very complex containing aliphatic, aromatic, hetero-atom and polar fractions. The main aromatic compounds found in the oil are benzene, toluene, xylenes, styrene, limonene and indene and their alkylated homologues and polycyclic aromatic hydrocarbons from two to 5 rings. The main aliphatic compounds are alkanes, with straight chain hydrocarbons from C_6- C_{37} and lower concentrations of alkenes. Determination of the fuel properties of tyre pyrolysis oils shows that they are similar to a gas oil (Diesel fuel) or light fuel oil and have been successfully combusted in test furnaces or blended with Diesel fuel and used in Diesel engines. The char yield from pyrolysis of tyres is high (~40wt.%), because the char contains the carbon black used in the formulation of the

original tyre. The chars have a high ash content(up to 15 wt.%). There has been several studies in trying to upgrade the char to higher quality carbon black or upgrading the char using steam or carbon dioxide as activating agents to produce activated carbons, with surface areas approaching commercial grades (~1000 m^2 g^{-1}). The main gas components from tyre pyrolysis are H_2, CH_4, C_2H_6, C_2H_4, C_3H_8, C_3H_6, C_4H_{10}, C_4H_8, C_4H_6, CO_2, CO and H_2S. Gas yield is known to increase with increasing pyrolysis temperature. There has been research into the use of low temperature Zeolite type catalysts to increase the concentration of valuable, single ring aromatic compounds in the product oils and substantial increases in concentration of benzene, xylenes and toluene have been reported. Nickel based catalysts at higher temperatures have been investigated with the aim of producing high yields of hydrogen from waste tyres. A large number of companies have developed tyre pyrolysis technologies, from batch reactors with typical throughputs of 1-2 tonnes per day to continuous systems, most commonly rotary kiln reactors, with planned throughputs of several hundred tonnes per day.

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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.

Table 2

Range of pyrolysis reactors and product yield from the pyrolysis of waste tyres

Reactor	Experimental conditions	Maximum Oil Yield				References
		Temperature (°C)	Oil (wt.%)	Char (wt.%)	Gas (wt.%)	
Fixed bed, batch	400-700 °C Temperature;	500	40.26	47.88	11.86	(Aydın and Ilkılıc, 2012)
Fixed bed, batch	500-1000 °C Temperature; 1200 min^{-1} heating rate	500	58.0	37.0	5.0	(Leung et al., 2002)
Closed batch reactor	350-450 °C; Temperature; 30 min^{-1} heating rate; 20 g tyre	450	~63	~30	~7	(Miranda et al., 2013)
Fixed bed, batch	300-720 °C Temperature; 5°C-80 °C min^{-1} heating rate; 50 g tyre	720	58.8	26.4	14.8	(Williams et al., 1990)
Fixed bed, batch	450-600 °C Temperature; 5°C min^{-1} heating rate; 3 kg, tyre	475	58.2	37.3	4.5	(Cunliffe and Williams, 1998a)
Fixed bed, batch	950 °C Temperature (max.); ~2°C min^{-1} heating rate; 1 tonne tyre	950[1]	20.9	40.7	23.9	(Williams et al., 1998)
Fixed bed, batch	350-600 °C Temperature; 5°C min^{-1} & 35 min^{-1} heating rate	400	38.8	34.0	27.2	(Banar et al., 2012)
Fixed bed, batch	300-700 °C Temperature; 15 °C min^{-1} heating rate; 175g tyre	700	38.5	43.7	17.8	(Laresgoiti et al, 2004)
Fixed bed, batch	375-500 °C Temperature; 10 °C min^{-1} heating rate; 10g tyre	425	60.0	~30	~10	(Kar, 2011)
Fixed bed, batch, internal fire tubes	375-575 °C Temperature; 750 g tyre	475	55	36	9	(Islam et al, 2011)
Moving screw bed	600-800 °C Temperature; 3.5 – 8.0 kg h^{-1} mass flow rate	600[2]	48.4	39.9	11.7	(Aylón et al., 2010)
Rotary kiln	550-680 °C Temperature; 4.8 kg h^{-1} throughput	550	38.12	49.09	2.39	(Galvagno et al., 2002)
Vacuum, conical spouted bed	425 °C & 500 °C Temperature; 25 & 50 kPa Vacuum	500	~60	~34	~4	(Lopez et al., 2010)
Rotary kiln	450-650 °C Temperature; 12-15 kg h^{-1} throughput	500	45.1	41.3	13.6	((Li et al., 2004))
Fluidised bed	740 °C Temperature; 1 kg h^{-1} throughput; tyre powder	740	30.2	48.5	20.9	(Kaminsky et al., 2009)
Fluidised bed	750-780 °C Temperature; 30 kg h^{-1} throughput; tyre pieces	750	31.9	38.0	28.5	(Kaminsky et al., 2009)
Fluidised bed	700 °C Temperature; 200 kg h^{-1} throughput; whole tyres	700[3]	26.8	35.8	19	(Kaminsky et al.,

						2009)
Fluidised bed	450-600 °C Temperature; ~220 g h⁻¹ throughput; tyre granules	450	55.0	42.5	2.5	(Williams and Brindle, 2003a)
Circulating fluidised bed	360-810 °C Temperature; 5 kg h⁻¹ throughput;	450	~52	~28	~15	(Dai et al., 2001)
Conical spouted bed	425 & 500 °C Temperature	500	~62	~35	~3	(Olazar et al, 2008)
Vacuum	485-550 °C Temperature; batch (80-180 Kg) & continuous	520[4]	45	36	6	(Roy et al., 1999)
Vacuum	500 °C Temperature: Pilot scale semi continuous	500	56.5	33.4	10.1	(Pakdel et al., 2001)
Vacuum	450-600 °C Temperature; batch (100 g)	550	47.1	36.9	16	(Zhang et al., 2008)
Drop tube reactor	450-1000 °C Temperature; 30 g h⁻¹ throughput	450[5]	37.8	35.3	26.9	(Conesa et al., 2004)
Fixed, wire mesh, fast reactor	390-890 °C Temperature; 70-90 °C s⁻¹ heating rate; 0.2 g	860	~5	~22	~73	(Zabaniotou and Stavropoulos, 2003)

[1] 12.9 wt% steel also produced; 950 °C was the maximum pyrolysis temperature

[2] Tyre mass flow rate of 8.0 kg h⁻¹.

[3] 13.3 wt% steel and 5.1 wt% water also produced

[4] Operated in batch mode; 10 wt.% steel and 3 wt.% water also produced

[5] Product yields average of two experiments.

Table 3

Oil composition from the pyrolysis of waste tyres (Williams and Bottrill, 1995; Cunliffe and Williams, 1998a; Dai et al., 2001; Li et al., 2004; Conesa et al., 2004; Laresgoiti et al., 2004; Olazar et al., 2008; Kaminsky et al., 2009; Banar et al., 2012).

Aliphatic Compounds	Single Ring Aromatic Compounds	Polyaromatic Hydrocarbons (PAH)	Others
Alkanes	Toluene	Naphthalene	Hydrocarbons
Decane (C_{10})	Ethylbenzene	Methylnaphthalene	Limonene
Undecane (C_{11})	Styrene	Biphenyl	Pinene
Dodecane (C_{12})	Xylene (1,2-dimethylbenzene)	Ethylnaphthalene	Cyclopentene, pentyl-
Tridecane (C_{13})	Xylene (1,3-dimethylbenzene)	Dimethylbiphenyl	Cyclohexene
Tetradecane (C_{14})	Xylene (1,4-dimethylbenzene)	Dimethylnaphthalene	Cyclohexene, propenyl-
Pentadecane (C_{15})	Toluene, ethyl	Acenaphthene	Cyclohexane, ethenyl-methyl-
Hexadecane (C_{16})	Benzene, propyl-	Trimethylnaphthalene	Cyclopentane, ethylidene-
Heptadecane (C_{17})	Benzene, ethyl-methyl-	Dihydromethylnaphthalene	Phenol
Octadecane (C_{18})	Methylstyrene	Tetrahydronaphthalene	Methylphenol
Nonadecane (C_{19})	Indene	Fluorene	Dimethylphenol
Eicosane (C_{20})	Benzene, butyl-	Methylfluorene	Isopropylphenol
Heneicosane (C_{21})	Benzene, dimethylpropyl-	Phenanthrene	Methylbenzaldehyde
Docosane (C_{22})	Benzene, dimethyl-	Anthracene	Tetradecanoic acid
Tricosane (C_{23})	Benzene, butenyl-	Dimethylfluorene	Pentadecanoic acid
Tetracosane (C_{24})	Benzene, pentyl-	Methylphenanthrene	Hexadecanoic acid
Pentacosane (C_{25})	Benzene, cyclopentyl-	Methylanthracene	Heptadecanoic acid
(C_{26}) - (C_{35})	Benzene, cyclohexyl-	Dimethlyphenanthrene	Octadecanoic acid
	Benzene, hexyl-	Fluoranthene	
Alkenes	Benzene, hexenyl-	Pyrene	Sulphur Compounds
Hexene	Methylindene	Trimethylphenanthrene	Thiophene
Heptene	Dimethylindene	Tetramethylphenanthrene	Benzothiophene
Octene	Benzene, methyl-butenyl-	Chrysene	Methylbenzothiophene
Nonene	Terphenyl	Benzo[a]pyrene	Dimethylbenzothiophene
	Dimethylindene	Benzo[e]pyrene	Trimethyldihydrobenzothiophene
	Trimethylindene	Benz[a]anthracene	Tetramethyldihydrobenzothiophene
	Ethylindene		Dibenzothiophene
			Naphthothiophene
			Methylnaphthothiophene
			Methyldibenzothiophene

Dimethyldibenzothiophene
Trimethyldibenzothiophene
Benzonaphthothiophene

Nitrogen Compounds
Aniline
Benzothiazole
Benzonitrile
Quinoline
Diphenylamine
Heptadecanenitrile
Dimethylquinoline

PCDD/PCDF
Hexachlorodibenzofuran
Heptachlorodibenzofuran
Octachlorodibenzodioxin

Table 4

Fuel properties of waste tyre pyrolysis oil.

Property	Reference (Williams et al. 1998)	Reference (Li et al., 2004)[1]	Reference (Banar et al., 2012)[2]	Reference (Murugan et al., 2008a)
Flash point (°C)	20	17.0	65	43
Carbon residue (%)	2.2	1.78	-	-
Density (kg L^{-1})	0.91	0.962	0.833	0.924
Viscosity cSt (at 40 °C)	6.30	-	-	3.77
Viscosity cSt (at 50 °C)	-	2.44	1.01	0.924
Viscosity cSt (at 60 °C)	2.38	-	-	-
Carbon (wt%)	88.0	84.26	79.61	-
Hydrogen (wt%)	9.4	10.39	10.04	-
Nitrogen (wt%)	0.45	0.42	0.94	-
Sulphur (wt%)	1.5	1.54	0.11	0.72
Oxygen (wt%)	0.5	3.39	9.3[4]	-
Initial B.Pt. (°C)	100	-	38.5	70
10% B.Pt (°C)	140	-	58.2	114.5
50% B.Pt. (°C)	264	-	174.8	296.1
90% B.Pt (°C)	355	-	-	386.4
Calorific value (MJ kg^{-1})	42.0	41.7	42.66	38
Ash (wt.%)	0.002	Tr	-	0.31
Moisture (%vol.)	4.6	0.88[3]	-	-

Tr = Trace

[1] Tyre oil produced at 500 °C

[2] Tyre oil produced at 35 °C min^{-1} heating rate

[3] Wt.%

[4] By difference

55

Table 5

Fuel properties of petroleum derived fuel oils (Harker and Backhurst, 1981).

Property	Kerosene	Gas Oil	Light Fuel Oil
Flash point (°C)	40	75	79
Carbon residue (%)	-	<0.35	-
Density (kg m^{-3})	0.84	0.78	0.89
Viscosity cSt (at 40 °C)	1.2	3.3	21
Carbon (wt%)	-	87.1	85.5
Hydrogen (wt%)	13.6	12.8	12.4
Nitrogen (wt%)	-	0.05	0.15
Sulphur (wt%)	0.1	0.9	1.4
Initial B.Pt. (°C)	140	180	200
50% B.Pt. (°C)	200	300	347
90% B.Pt (°C)	315	-	-
Calorific value (MJ kg^{-1})	46.6	46	44.8
Ash (wt.%)	-	0.01	0.02
Moisture (%vol.)	-	0.05	0.1

Table 6

Properties of tyre pyrolysis chars.

Property	Reference (Cunliffe and Williams, 1998b)	Reference (Conesa et al., 2004)	Reference (Li et al., 2004)	Reference (Galvagno et al., 2002)	Reference (Olazar et al., 2008)
Reactor	Fixed bed	Drop tube	Rotary kiln	Rotary kiln	Conical Spouted bed
Pyrolysis temperature	500 °C	450 °C	500 °C	550 °C	500 °C
Tyre	3 kg batch	30 g h^{-1} throughput	12-15 kg h^{-1} throughput	4.8 kg h^{-1} throughput	-
Proximate Analysis (wt.%)					
Moisture	0.4	0.37	2.35	3.57	-
Volatiles	2.8	7.78	16.14	12.78	-
Ash	11.6	8.27	12.32	15.33	-
Ultimate Analysis (wt.%, daf[1])					
Carbon	90.6	88.19	82.17	85.31	80.3
Hydrogen	0.9	0.6	2.28	1.77	1.3
Nitrogen	0.7	0.1	0.61	0.34	0.3
Sulphur	2.3	1.9	2.32	2.13	2.7
Chlorine	0.08	-	-	-	-
Calorific value (MJ kg^{-1})	30.5	30.8	31.5	30.7	29.3
Surface area (m^2 g^{-1})	64	93	-	-	83
Metals (wt.%)					
Zn	4.1	6.68	-	4.06	3.8
Ca	1.2	0.13	-	-	-
Fe	0.2	0.04	-	0.54	-
Al	0.15	-	-	1.09	-
Si	0.42	1.69	-	-	-
Pb	-	0.01	-	tr	-

[1] daf = dry ash-free

Table 7

Gas composition from the pyrolysis of waste tyres (wt% of tyre mass).

Reactor	Temperature (°C)	Gas Composition												References
		H_2 (wt%)	CH_4 (wt%)	C_2H_6 (wt%)	C_2H_4 (wt%)	C_3H_8 (wt%)	C_3H_6 (wt%)	C_4H_{10} (wt%)	C_4H_8 (wt%)	C_4H_6 (wt%)	CO_2 (wt%)	CO (wt%)	H_2S (wt%)	
Fluidised bed 0.2 kg h^{-1} throughput	450	0.06	0.29	0.17	0.24	0.16	0.04	Tr	0.08	1.26	Tr	Tr	-	(Williams and Brindle, 2003a)
Fluidised bed 0.2 kg h^{-1} throughput	600	0.24	2.39	0.74	3.84	0.40	1.92	Tr	0.26	2.60	Tr	Tr	-	(Williams and Brindle, 2003a)
Fluidised bed 1.4 kg h^{-1} throughput	598	0.59	2.9	1.2	1.6	0.76	2.2	0.41[1]	5.75[2]	0.74	1.8	1.6	0.38	(Kaminsky et al., 2009)
Fluidised bed 1.4 kg h^{-1} throughput	650	0.72	4.0	1.4	2.5	0.69	3.0	0.37[1]	5.87[2]	1.11	2.1	1.4	0.5	(Kaminsky et al., 2009)
Fluidised bed 1.4 kg h^{-1} throughput	700	1.1	6.9	1.8	4.0	0.63	4.4	0.31[1]	6.76[2]	1.7	2.5	2.1	0.6	(Kaminsky et al., 2009)
Fixed bed, batch	500	0.2	0.8	0.3	1.2	0.3	0.5	0.2[1]	0.3[2]	1.9	0.3	0.1	-	(Williams and Brindle, 2003b)
Drop tube reactor[3]	450	0.05	0.65	0.24	0.59	0.09	0.22	0.01[1]	0.02[2]	0.01	3.37	-	-	(Conesa et al., 2004)
Drop tube reactor[3]	750	0.35	4.62	1.11	2.42	0.14	1.11	0.03	0.01	0.18	4.11	0.60	-	(Conesa et al., 2004)
Drop tube reactor[3]	1000	1.00	7.89	0.10	0.71	Tr	0.03	-	-	0.01	1.81	1.32	-	(Conesa et al., 2004)
Rotary kiln	600	1.4	1.11	0.67	0.67	-	-	-	-	-	0.70	0.31	0.21	(Galvagano et al, 2002)
Moving screw bed	600	~0.7	3.6	-	-	-	-	-	-	-	-	-	1.4	(Aylón et al., 2010)
Moving screw bed	800	~1.8	13.8	-	-	-	-	-	-	-	-	-	0.8	(Aylón et al., 2010)

Tr = Trace
[1] Iso-butane and n-butane gases
[2] Trans-2-butene, 1-butene, iso-butene, cis-2-butene gases
[3] Data are the average of two experiments

Table 8

Examples of commercial and semi-commercial tyre pyrolysis systems

Company	Location	Reactor Type	Capacity	References
Splainex Ltd	Hague, Netherlands	Rotary kiln	~20 tonnes day^{-1}	(Splainex, 2013)
Xinxiang Doing Renewable Energy Equipment Co., Ltd	Xinxiang, China	Rotary kiln	6-10 tonnes day^{-1}	(Xinxiang Doing, 2013)
RESEM	Shangqui, China	Rotary kiln	8-20 tonnes day^{-1}	(RESEM, 2013)
Kouei Industries	Vancouver, Canada	Fixed bed/Batch	16 tonnes day^{-1}	(Kouei Industries, 2013)
DG Engineering	Gummersbach, Germany	Rotary kiln	~10 tonnes day^{-1}	(DG Engineering, 2013)
FAB India	Amedabad, India	Rotary kiln	5-12 tonnes day^{-1}	(FAB India, 2013)
Octagon Consolidated	Selangor, Malaysia	Rotary kiln	2.4-120 tonnes day^{-1}	(Octagon Consolidated, 2013)
No-Waste Technology	Reinach, Germany	Fixed bed/Batch	4 tonnes day^{-1}	(No-Waste Technology, 2013)
PYReco	Teeside, UK	Rotary kiln	200 tonnes day^{-1}	(PYReco, 2013)
Pyrocrat Systems	Navi Mumbai, India	Rotary kiln	2-10 tonnes day^{-1}	(Pyrocrat Systems, 2013)