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# Catalytic co-pyrolysis of biomass and waste plastics as a route to upgraded bio-oil

Andrew C. Dyer, Mohamad A. Nahil, Paul T. Williams*

School of Chemical and Process Engineering, University of Leeds, Leeds, LS2 9JT, U.K.

(*Corresponding author; Email; p.t.williams@leeds.ac.uk; Tel; #44 1133432504)

## ABSTRACT

A two-stage reactor system consisting of co-pyrolysis of biomass and plastic in the 1st stage and catalytic upgrading (zeolite ZSM-5 catalyst) of the derived pyrolysis gases in the 2nd stage was used to investigate the yield and composition of the product gases and bio-oil. Biomass waste wood and waste plastics in the form of high density polyethylene, low density polyethylene, polypropylene, polystyrene and polyethylene terephthalate were used as feedstock. The addition of the plastics to the biomass with co-pyrolysis-catalysis, produced a higher $C_nH_m$ gas yield compared with what would be expected by calculation, suggesting some interaction of the biomass and plastic. The presence of waste plastic resulted in a decrease in the relative proportion of oxygenated compounds in the product oil compared to pyrolysis of biomass alone; for example a reduction of >65% for biomass with polyethylene and polypropylene and >95% reduction for biomass with polystyrene. The fuel properties of the co-pyrolysis upgraded oil were improved compared to biomass alone; for example, the co-pyrolysis of polystyrene and biomass showed an improved relative proportion of compounds in the $C_5$ — $C_{12}$ fuel range (76%). In terms of the ratio of biomass to plastic, even low quantities of plastic (9:1 biomass:plastic ratio) produced a lower relative proportion of oxygenated bio-oil compounds, for example biomass:polystyrene at a ratio of 9:1 reduced the relative proportion of oxygenated compounds in the product bio-oil by >55%.

**Keywords**: Pyrolysis; Biomass; Plastics; Zeolite; Bio-oil

## 1. Introduction

There is a global drive towards developing a low carbon future and a reduction in greenhouse gas emissions. Such a challenging low carbon scenario implies alternative and sustainable development of novel energy systems and also alternatives to the traditional use of fossil fuels. The prevalence of liquid fuelled vehicles globally is likely to remain high and alternatives to petroleum based liquid fuels is imperative [1]. Pyrolysis of biomass is a technology that has the potential to produce liquid fuels capable of replacing or supplementing liquid petroleum based fossil fuels. The process involves heating of the biomass feedstock to a temperature of ~500 °C followed by quenching of the evolved pyrolysis gases to obtain bio-oil [2]. However, oils produced from pyrolysis of biomass have several qualities which make them unsuitable for replacing liquid fuels, including chemical complexity, high moisture content, high oxygen content, acidic properties, and tendency to polymerise [3,4]. Of particular importance for the liquid fuels sector are processes that can produce products derived from biomass that can directly enter the existing petroleum refinery infrastructure. Production of a low oxygen bio-oil produced from biomass with a composition similar to petroleum crude enables direct refining of the oil in existing petroleum refineries. Therefore, the upgraded bio-oil does not require special infrastructure or vehicles to transport, store, or process the bio-oil and the refined product can directly substitute into the existing petroleum refinery infrastructure [5,6].

Removal of oxygen from the crude biomass pyrolysis oil is commonly by either hydro-deoxygenation involving input hydrogen and moderate to high pressure or via catalytic deoxygenation, typically involving zeolite catalysts through catalytic cracking, decarboxylation, decarbonylation and dehydration reactions [5]. The addition of hydrogen to the zeolite catalytic deoxygenation process has also been suggested [3].

An alternative option is to introduce hydrogen to the process through the co-pyrolysis of a material such as waste plastics which are rich in hydrogen, that is, plastics with a high H/C ratio such as polyethylene, polypropylene and polystyrene [1,7]. It is suggested that the presence of the hydrogen-rich plastic serves to donate hydrogen during co-pyrolysis with biomass resulting in an upgrading of the bio-oil quality [8]. Alam et al [9] have reported that increasing the H/C ratio alters the reaction mechanism of oxygen removal by promoting dehydration reactions at the expense of decarbonylation and decarboxylation reactions. There have been several reports into the co-pyrolysis of biomass and waste plastics with the aim of upgrading the product bio-oil by deoxygenation [10-14].

The introduction of zeolite catalysts to the co-pyrolysis of biomass and waste plastics has further developed the process. For example, the catalytic co-pyrolysis of lignocellulosic biomass and plastics has been reviewed by Zhang et al [15]. They concluded that co-pyrolysis produces a product oil that is enhanced in aromatic content, particularly mono-aromatic compounds. They also reported a lowered catalyst coke formation during co-pyrolysis. Zhang et al [15] also produced a reaction scheme for catalytic co-pyrolysis of plastics with lignocellulosic biomass. Both the plastics and biomass polymers crack to produce small compounds involving short chain alkenes and furan derivatives from cellulose and hemicellulose which then react together to produce non-oxygenated aromatic compounds. Xue et al [14] reported on the co-pyrolysis of polyethylene with model biomass constituents (cellulose, hemicellulose and lignin) in the presence of HZSM-5 zeolite catalyst. They showed that there was an increase in aromatic hydrocarbons yield and lower coke formation on the catalyst compared with catalytic pyrolysis of the plastic and biomass separately. Uzoejinwa,et al [11] also considered catalytic co-pyrolysis as a route to enhance bio-oil product quality in their review of biomass and plastics pyrolysis. They also reported the enhanced production of aromatic compounds during catalytic co-pyrolysis and also reported increased efficiency of the conversion process due to lowered activation energy and process temperature. Li et al [16] investigated the catalytic-co-pyrolysis of biomass (cellulose, lignin and pine wood) and waste plastics (polyethylene, polypropylene and polystyrene) using ZSM-5 zeolite catalyst. They reported that the highest synergistic effect of increased aromatic content was for cellulose/wood and polyethylene during catalytic co-pyrolysis.

The reported research suggests that there is a synergistic effect between biomass and plastics during co-pyrolysis with zeolite catalysis that has a beneficial effect on the composition of the product oil, with an upgrading of the quality of the oil compared to lignocellulosic biomass pyrolysis bio-oil. Most of the previous research work has concentrated on pure plastics, and mainly work has been carried out on polyethylene. However, the most common post-consumer plastics are polyethylene (high density polyethylene (HDPE) and low density polyethylene (LDPE), polypropylene (PP), polystyrene (PS) and polyethylene terephthalate (PET) and are most likely to contain contaminants. In this work, we report on the catalytic co-pyrolysis of 'real-world' waste plastics (HDPE, LDPE, PP, PS, and PET) produced from a waste plastics recycling company that are co-processed with waste biomass. The aim of the research was to improve the quality of the product bio-oil by deoxygenation using the plastics as a source of hydrogen together with zeolite ZSM-5 catalytic upgrading. Detailed analysis of the product oils and gases is presented.

## 2. Materials and Methods

*2.1. Materials*

The biomass used was in the form of wood pellets produced as compressed sawdust pellets from waste wood and supplied by Liverpool Wood Pellets Ltd, Liverpool, UK. The waste wood pellets were milled and sieved to produce a feedstock for experiments of size range between 1.0 - 2.8 mm. The waste plastics (HDPE, LDPE, PP, PS, and PET) were supplied as recycled waste plastic as ~2 mm sized pellets by Regain Polymers Limited, Castleford, UK. The biomass and plastics were intimately mixed for the experiments. The proximate analysis of the waste plastics and biomass was carried out using British Standards BS-EN-14774-3, BS-EN-15148 and BS-EN-14775. Elemental analysis for carbon, hydrogen, nitrogen and sulphur was determined using a CE Instruments Flash EA2000 and also including separate analysis for oxygen (rather than by difference). The results are shown in Table 1. The biomass contained 7.8 wt.% moisture which was not observed in the plastic samples. Also, the waste plastics showed a significant content of ash at, 0.3 wt.% for LDPE, 0.8 wt.% for PP and 1.6 wt.% for PS,4.1 wt.% for HDPE and 42.7 wt.% for PET. This data reflects the fact that the plastics are real-world waste plastics and not virgin materials, the ash content comprising dirt or perhaps filler material. In particular, the PET contained a high content of $SiO_2$ present as filler in the PET. In addition, the presence of oxygen in the HDPE, LDPE, PP and PS samples also indicates some form of contamination, perhaps from the presence of oxygenated plastics such as polyethylene terephthalate (PET).

The catalyst used for the investigation was a zeolite ZSM-5 catalyst supplied by Nankai University Catalyst Co. Ltd, Tianjin, PR China. The catalyst had a surface area of 282 $m^2 g^{-1}$, micropore volume of 0.26 $cm^3 g^{-1}$ and the silica: alumina ratio was 38:1.

### *2.2. Catalytic co-pyrolysis reactor system*

The pyrolysis experiments were carried out using a two stage fixed bed reactor system constructed of stainless steel and externally heated by two separately heated and controlled electrical furnaces. A schematic diagram of the reactor system is shown in Figure 1. The first stage reactor was where co-pyrolysis of the biomass and plastics took place. The evolved pyrolysis gases were passed directly to a second stage catalytic reactor where catalysis of the derived gases took place in the presence of the zeolite ZSM-5 catalyst. Each experiment used 2.0 g of the biomass/plastic sample (1:1 ratio) suspended in a stainless steel crucible in the pyrolysis reactor. The catalyst reactor used 4.0 g of the ZSM-5 as a catalyst bed supported on quartz wool. Therefore, the feedstock:catalyst ratio was 1:2. Thermocouples measure the temperature in each part of the reactors to allow for heating control in each reactor. Nitrogen was used as the purge gas to carry the evolved gases through the reactor stages and condensation system. After the reactors, the gases were passed through a water cooled and two dry-ice cooled condensers to condense the product oils. The non-condensable gases were passed to a 25 litre Tedlar™ gas sample bag. The experimental procedure consisted of pre-heating the catalyst reactor to 500 °C, once a stable temperature was achieved in the catalyst stage, the first stage pyrolysis reactor containing the biomass/plastic mixture was heated at a heating rate of 10 °C $min^{-1}$ to 500 °C. At the end of each experiment the condensed product oils were collected from the condensers and analysed off-line by coupled gas chromatography-mass spectrometry and the gases collected in the gas sample bag were analysed off-line by packed column gas chromatography. The experiments conducted consisted of pyrolysis of biomass without the

ZSM-5 catalyst with sand in place of the catalyst as a 'blank', biomass pyrolysis with ZSM-5 catalyst, pyrolysis of individual plastics with ZSM-5 and pyrolysis of 1:1 mixtures of biomass with the individual plastics with ZSM-5 catalyst.

The method used for determining mass balance involved weighing the feedstock crucible from the pyrolysis reactor before and after each experiment to determined the mass of char and the condensers were weighed before and after to give the mass of liquid. The mass of gas was determined by the volumetric gas concentrations of the individual product gases obtained from gas chromatography analysis calibrated with standard gas mixtures, followed by calculation of the  mass of gas based on the nitrogen gas flow rate and the ideal gas law. Repeatability tests with the two-stage pyrolysis-catalysis experimental reactor system were carried out using the biomass as the test feedstock and showed that the standard deviation for the mass balance was 0.3 wt.% for char, 1.2 wt.% for liquid and 1.1 wt.% for gas yields.

### *2.3. Gas analysis*

The product gases collected in the gas sample bag were analysed using three separate gas chromatographic (GC) instruments. The first GC was a Varian CP-3380 used for the analysis of the permanent gases ($H_2$, $O_2$, $N_2$ and CO) with a 2 metre x 2mm column packed with a 60-80 mesh molecular sieve, argon carrier gas and with a thermal conductivity detector (TCD). The second GC was also a Varian CP-3380, using a Hyesep 60-80 mesh molecular sieve column, Ar carrier gas with a TCD and was used for analysis of $CO_2$ ($CO_2$ was analysed separately because of the co-elution of CO and $CO_2$) using a different GC oven temperature programme compared with the permanent gas analysis. A third Varian

CP-3380 instrument was equipped with a 2 metre x 2mm stainless steel column packed with Hyesep 80-100 mesh packing, $N_2$ carrier gas an flame ionisation detection (FID) and analysed the hydrocarbon gases (methane, ethane, ethene, propane, propene, butane, butene and butadiene). Calibration of each GC used known gas standards which gave response factors (RF) and retention times for each gas.

### *2.4. Oil analysis*

The oil from the pyrolysis reactions collected in the condenser system was diluted using 10ml of dichloromethane (DCM) for the purpose of GC-mass spectrometry (GC-MS) analysis. Prior to GC-MS injection the DCM was passed through a column containing 7.0 g of sodium sulphate to remove residual water. The GC-MS equipment used was a Varian CP-3800 GC with Saturn 2200 MS containing a 30metre x 0.25 mm VF-5ms column. The resulting peaks measured by MS were compared to the NIST compound library to identify the compounds present and the peak area was recorded for each compound. The GC-MS was calibrated with a wide range of aromatic and oxygenated hydrocarbon compounds to enable identification of the peak areas of the eluted compounds. The designated peak areas of the total ion chromatograms were used to characterise different categories of compounds; aromatic and aliphatic containing structured compounds; oxygenated and non-oxygenated compounds, carbon number range $C_5$ — $C_{12}$ and $\geq C_{13}$; 1 — 4 ring aromatic compounds and linear aliphatic structured compounds. It should be noted that each category is not mutually exclusive, in that an individual compound may contain an aromatic ring and be categorised as aromatic containing structured compound, but also may contain an oxygen atom and be categorised as oxygenated. Such a compound may also lie in the $C_5$

— $C_{12}$ carbon number range and be a two-ring compound. However, the analysis gives an overview of the influence of biomass:plastic co-pyrolysis with zeolite ZSM-5 catalytic upgrading in terms of a semi-quantitative bio-oil composition.

### *2.5. Catalyst analysis*

The used ZSM-5 catalyst after reaction in the pyrolysis-catalyst reactor was investigated to determine the extent of catalyst carbon deposits (coke) using temperature programmed oxidation (TPO). The method involves heating the used catalyst in a thermogravimetric analyser (TGA) in an air atmosphere and the weight loss due to oxidation of the carbon on the catalyst determined in relation to the rise in temperature. The TGA used was a Mettler Toledo TGA/DSC3+ TGA with an oven heating temperature programme of heating rate of 15 °C min$^{-1}$, from room temperature to a 800 °C and hold time of 10 minutes.

## **3. Results and Discussion**

### *3.1 Pyrolysis-catalysis of waste biomass and individual waste plastics*

Table 2 shows the product yields for char, oil and gas from the two-stage, pyrolysis-catalysis (zeolite ZSM-5) of biomass, biomass with sand as a blank catalyst material and from the pyrolysis-catalysis (zeolite ZSM-5) of the individual waste plastic samples. Biomass pyrolysis in the absence of the ZSM-5 catalyst produced a high liquid yield of 56.3 wt.%, but when the ZSM-5 catalyst was introduced, the liquid yield reduced to 49.3 wt.% with a consequent increase in gas yield due to cracking of the biomass pyrolysis gases. The residual char yield remained constant at ~25 wt.%, since it would be unaffected by any process parameters in the 2nd stage catalytic reactor. Figure 2 shows the analysis of the product gases from the pyrolysis and catalytic pyrolysis of the biomass, showing that the main gases were CO and $CO_2$ with lower concentrations of $CH_4$, $H_2$ as well as $C_nH_m$ hydrocarbon gases. The influence of the presence of the catalyst was to produce a higher yield of CO and $CO_2$, illustrating the elimination of oxygen as the $CO_x$ gases. Water is also likely to be a product of oxygen removal by zeolite catalysis, but would be able to be differentiated from the product water from biomass pyrolysis process. Figure 2 shows that the hydrocarbon gases are increased in the presence of the ZSM-5 catalyst due to cracking reactions which produce short chain unsaturated hydrocarbons from saturated hydrocarbons. Table 2 also shows the product yield from the pyrolysis-catalysis of the individual waste plastics. The results show that the pyrolysis-catalysis of the plastics produces a mainly gas and oil product. The pyrolysis-catalysis of PET resulted in a high residual char yield produced from the pyrolysis process, but the char also contained a high content of $SiO_2$ filler material. The high content of inorganic material in the PET sample was linked to the real-world nature of the waste PET sample, which contained a high content of reinforcement filler material. It can be noted that for LDPE, PET, PP and PS, the residual char yield was slightly less than the ash content of the residual plastic feedstock, most probably due to the experimental variation in the proximate analysis of the feedstock and the experimental procedure of the pyrolysis-catalysis experiments. The presence of inorganic material in the feedstock biomass and plastics may influence the co-pyrolysis-catalytic process. For example, it has been reported that volatile metals, particularly alkali and alkaline earth metals present in biomass can deactivate ZSM-5 catalyst which poison or block the active sites of the catalyst during the pyrolysis-catalytic process [17]. The presence of inorganic material in the plastic feedstock as a contaminant of the real-world waste plastics may also present an issue of catalyst deactivation if the inorganic material contains volatile metal species. However, the presence of the volatile metals in the ash, may also initiate a positive effect, since it has also been reported that the alkali and alkaline earth metals can catalyse the cracking and thermolysis reactions in the pyrolysis vapour phase and result in changes in the liquid product composition [17].

Figure 3 shows the gas composition produced from the individual waste plastics using the pyrolysis-catalysis system with ZSM-5 catalyst. The main gases produced from the pyrolysis-catalysis of the polyalkene plastics, HDPE, LDPE and PP, were $C_nH_m$ hydrocarbon gases which were mainly $C_2$ — $C_4$ alkane and alkene gases, produced from the catalytic cracking of the polymer pyrolysis fragments. Pyrolysis-catalysis of PET produces mainly CO and $CO_2$ product gas derived from the catalytic degradation of the oxygenated hydrocarbon groups in the PET polymer [18]. The pyrolysis-catalysis of polystyrene produces a mainly liquid product at 86.4 wt.% (Table 2) with a gas yield consisting of $C_1$ — $C_4$ hydrocarbons.

Table 3 shows the composition of the product oil from the pyrolysis-catalysis (ZSM-5) of biomass (BMS) and the individual plastics. The product oils were characterised in relation to their content of; aromatic and aliphatic containing structured compounds; oxygenated and non-oxygenated compounds, carbon number range $C_5$ — $C_{12}$ and $\geq C_{13}$; 1 — 4 ring aromatic compounds and linear aliphatic structured compounds. Also shown in Table 3 is the pyrolysis of biomass with sand in place of the catalyst. It is clear that the uncatalysed pyrolysis of the biomass produces a product oil, which contains almost entirely oxygenated compounds (99.8%). However, the introduction of the ZSM-5 catalyst to the reactor system reduced the oxygenated compounds to 37.3 wt.% of the product oil. Zeolite ZSM-5 catalysts are alumina-silicates with a three-dimensional tetrahedral porous structure that have been shown to de-oxygenate the oxygenated compounds in the bio-oil to hydrocarbons in the $C_1$ — $C_{10}$ range with the oxygen eliminated as $CO_2$, CO and $H_2O$ [19,20]. The condensed hydrocarbon product oil contains aromatic structured compounds including single-ring and two-ring aromatic structured compounds such as, benzene, toluene, alkylated benzenes, naphthalene and alkylated naphthalenes and in addition, higher molecular weight polycyclic aromatic hydrocarbons [19]. The data for biomass in relation to the high content (94.4%) aromatic structured containing compounds reflects the complex nature of the ZSM-5 upgraded bio-oil containing compounds with oxygen, aromatic structures and aliphatic structures. As noted before, each category of compounds shown in Table 3 is not mutually exclusive, compounds containing an aromatic ring may also be classified as oxygenated. The $C_5$ — $C_{12}$ carbon number range of the biomass pyrolysis oil was 98.2%, suggesting that the sand acted to thermally crack the biomass pyrolysis gases and the effect of the ZSM-5 was to only slightly further increase the gas cracking.

Table 3 also shows the characterisation of the product oil from the pyrolysis-catalysis of the individual plastics. It has been reported previously [21] that the pyrolysis of polyalkene plastics, including HDPE, LDPE and PP produces a mainly aliphatic wax/oil product. Table 3 shows that with the addition of the ZSM-5 zeolite catalyst, the high molecular weight aliphatic compounds are degraded/cracked to produce oils with lowered hydrocarbon number range and composed of aliphatic and aromatic hydrocarbons, including benzene, toluene, ethylbenzene, xylenes and styrene [18]. Pyrolysis of PET produces a liquid reported to contain mainly terephthalic acid and benzoic acid and gaseous

CO and $CO_2$ derived from the oxygenated hydrocarbon groups in the polymer. Addition of the ZSM-5 catalyst the terephthalic acid and benzoic acid are reported to be reduced to produce benzene and toluene, but high yields of CO and $CO_2$ [18]. Pyrolysis of polystyrene produces an oil product consisting largely of styrene and styrene oligomers but with the addition of zeolite catalyst, the oil yield remains high but styrene and other single ring aromatic hydrocarbons including benzene and toluene are the main components and the gas yield is slightly increased [18,22].

## 3.2 Pyrolysis-catalysis of biomass:plastic mixtures

Table 4 shows the product yield from the co-pyrolysis of the biomass: plastic mixtures (1:1 ratio) with the individual plastics followed by catalysis with the ZSM-5 catalyst. The polyalkene waste plastics (HDPE, LDPE and PP) produced quite similar results with a char yield ranging from 13.1 to 15.1 wt.%, liquid yield between 51.6 and 56.0 wt.% and gas yield 31.4 to 36.6 wt.%. Examining the expected yields based on the data from Table 2 for the separate pyrolysis-catalysis of the biomass and the individual polyalkene plastics data shown in Table 4, the results show that there was evidence of some interaction between the materials (Table 5). The addition of the plastics to the biomass, in most cases produced a higher gas yield and lower liquid yield compared with what would be expected by calculation (Table 5). For example, the gas yield from the biomass:LPDE mixture was 36.6 wt.%, but from Table 2 a gas yield of 29.1 wt% would be expected and for biomass:PP the gas yield was 35.9 wt.% but the calculated expected value was 29.4 wt.%. However, for the biomass:PET and biomass:PS results the experimental gas yield was less than would be expected by calculation.

The yield and composition of the gases produced from the pyrolysis-catalysis of the biomass:plastic mixtures in the presence of the ZSM-5 catalyst are shown in Figure 4. The gases represent pyrolysis-catalysis of the biomass and the individual plastics. For example, the biomass and polyalkene plastic mixtures (HDPE, LDPE and PP) are dominated by hydrocarbons (mainly $C_2$ — $C_4$) derived from the plastics and CO and $CO_2$ from the biomass. In fact, the $C_nH_m$ hydrocarbons for the biomass:polyalkene plastic mixtures were significantly higher than would be expected based on individual gas yield data from Figure 2 and Figure 3, suggesting interaction between the biomass and the HDPE, LDPE and PP to produced more hydrocarbons.  This was also the case for the biomass:PET and biomass:PS mixtures, but to a lesser extent.

Table 6 shows the relative proportion of compounds in the upgraded bio-oil from the biomass:plastic co-pyrolysis-catalysis  in the presence of zeolite ZSM-5 catalyst which were categorised as aromatic/aliphatic, oxygenated, in the fuel range $C_5$ — $C_{12}$ and $\geq C_{13}$ and/or 1 — 4 ring aromatic/linear aliphatic. Each different category of compounds was normalised to 100%. The results show that the presence of the plastics during co-pyrolysis with the biomass significantly reduces the relative proportion of oxygenated compounds in the product oil compared to the bio-oils produced from biomass pyrolysis. For example the relative proportion of oxygenated compounds compared to non-oxygenated compounds in the product oil was 99.8% (with sand) and with biomass pyrolysis-catalysis at 37.3% and then to between 2.1% and 19.3% depending on the type of plastic used with the biomass. The addition of the polyalkene plastics (HDPE, LDPE, PP) to the biomass produced an upgraded bio-oil with the relative proportion of oxygenated compounds comprising 10.2% — 12.3%. The biomass:polyalkene plastic co-pyrolysis-catalysis upgraded bio-oil also shows that the oil is a mixture of compounds with aromatic and aliphatic structured containing mainly single ring aromatic compounds and linear aliphatic compounds, mostly in the $C_5$ — $C_{12}$ carbon number fuel range. The upgraded bio-oil from co-pyrolysis-catalysis of biomass and PS produced a product oil with a very low relative proportion of oxygenated compound content (2.1%) and comprised of 95.6% aromatic ring containing compounds. The oil was also mainly in the $C_5$ — $C_{12}$ fuel range with a high content of 1 — 4 ring aromatic compounds. The biomass:PET co-pyrolysis-catalysis oil was highly aromatic with a high content of compounds in the $C_5$ — $C_{12}$ carbon number fuel range. The relative proportion of oxygenated compounds in the product oil was 19.7% reflecting the oxygen content of both feedstocks.

The process system used in this work comprises co-pyrolysis in the first stage reactor followed by catalysis of the evolved gases/vapours derived from the pyrolysis of both biomass and the plastic components of the mixture. Therefore, there will be the potential for interaction of the two feedstocks within the first stage pyrolysis process and also interaction of the gases/vapours over the second stage zeolite catalysis. Thermogravimetric analysis has been used extensively to investigate the thermal degradation of biomass and plastics [23-25]. A wide range of lignocellulosic biomass for example, coconut shell, baggasse, rice husks, cotton stalk, palmshell, bamboo and pine wood sawdust thermally degrade over a temperature range of ~200 °C — 550 °C [23,24]. However, the individual thermogravimetric degradation profile of each biomass type will depend on the particular macro-biopolymer composition. The main biopolymers, in biomass, hemicellulose, cellulose and lignin thermally degrade over different temperatures within the 200 °C — 550 °C range.

Hemicellulose typically thermally degrades between 200 °C — 330 °C cellulose between 330 °C — 450 °C and lignin between 250 °C — 550 °C, with some variation due to the particular composition of the biopolymer [24,26]. The thermal decomposition of plastics determined from thermogravimetric analysis also depends on the type of plastic polymer. High density polyethylene, low density polyethylene and polypropylene typically decompose between temperatures of 430 °C — 520 °C, polyethylene terephthalate between 370 °C — 460 °C and polystyrene between 410 °C — 470 °C [8,24,27]. Again, there will be some variation between the thermal degradation of particular polymers due to their particular characteristics and whether they are pure or recycled polymers [27]. Therefore, the level of interaction of the biomass and plastics during the pyrolysis stage will depend on the composition of the biomass and the particular plastic under investigation. For example, the hemicellulose and most of the cellulose will have decomposed and the volatiles exited from the pyrolysis stage before polyethylene (HDPE and LDPE) and polypropylene have completed their decomposition. However, the volatiles from polystyrene pyrolysis decomposition would be available for interaction with the volatiles from hemicellulose, cellulose and also lignin. Li et al [28] investigated the thermal decomposition of cellulose and low density polypropylene using thermogravimetric analysis. They reported no interaction between the two feedstocks due to the different temperatures of devolatilisation. Zhou et al, [8] used TGA to investigate the interaction of biomass (pine sawdust) and LDPE, HDPE and PP. They showed that biomass starts to decompose at 250 °C whilst the plastics start to decompose at 400 °C. They reported interaction of the biomass and plastics devolatilisation occurred at higher temperatures of the TGA. Oyedun et al [23] investigated the thermogravimetric decomposition of mixtures of biomass with polystyrene and polyethylene, they reported that polystyrene had a greater interaction with the biomass, particularly the lignin component of biomass, compared to polyethylene because of the overlapping temperatures of decomposition. Gunasee et al [29] used a TGA system and also a fixed bed pyrolysis reactor to investigate the interaction of biomass (cellulose) and plastics (LDPE). TGA experiments showed clearly that cellulose decomposed at low temperature with a maximum peak of decomposition at 340 °C whereas the LDPE peak decomposition occurred at 480 °C. They reported no indication of synergistic effects between the cellulose and LDPE, since the cellulose would have volatilised well before the decomposition of the LDPE. However, when they used the fixed bed reactor involving significantly larger amounts of feedstock (~20 g) they reported synergistic effects, which were related to the interaction of the LDPE and cellulose derived char during the pyrolysis process. A synergistic interaction between biomass and plastics has been reported by others. Ryu et al [1] reported that biomass degradation commences before high density polyethylene, but the decomposition process of the biomass releases radicals that initiate the depolymerisation of the HDPE. Yuan et al,[30] also reported that hydrogen from HDPE decomposition can promote cellulose decomposition and oxygen compounds derived from the cellulose decomposition promoted HDPE cracking.

After the co-pyrolysis stage of the process, the pyrolysis vapours from the biomass and plastics enter the second catalytic stage reactor and have the potential to interact with the zeolite ZSM-5 catalyst. Zeolite acid catalysts promote dehydration, decarbonylation and cracking reactions, but also importantly the zeolite ZSM-5 aromatisation reaction [1,10,31]. During co-pyrolysis of biomass and plastics, aromatisation is promoted via the Diels-Alder reaction between alkenes derived from plastics, particularly polyalkene plastics such as HDPE, LDPE and PP, and biomass (cellulose and hemicellulose) derived furans. Aromatic forming reactions involving lignin follow a pathway of phenolic compounds and hydrogen abstraction from the polyalkene plastic [1].

Zhang et al [32] used a pyroprobe-GC-MS to investigate the co-pyrolysis of biomass (corn stalk) and plastic (HDPE) in the presence of a HZSM-5 zeolite catalyst. The mixture of biomass and plastic was placed in the pyroprobe and ZSM-5 placed either side of the mixture, separated by quartz wool. Therefore, the biomass and plastics were pyrolysed and the evolved gases passed through the ZSM-5 catalyst bed as a two-stage system. They showed that co-pyrolysis-catalysis of the biomass and plastic increased the yield of hydrocarbons, demonstrating a synergistic effect. Lin et al, [33] also used a pyroprobe-GC-MS with separation of the feedstock and catalyst using quartz wool. The feedstock was a mixture of wood (poplar) and plastic (HDPE) prepared to produce a composite material. Several different zeolite catalysts were investigated. The introduction of the HZSM-5 catalyst produced a marked increase in aromatic content of the product hydrocarbons, particularly, benzene, xylenes, toluene and naphthalenes. There was a corresponding decrease in the yield of oxygenated compounds such as methylglyoxal, acetic acid and phenol. They also noted that the conditions of pyrolysis such as pyrolysis temperature, heating rate, feedstock:catalyst ratio and catalyst type strongly influenced product hydrocarbon composition. Xue et al, [14] also used a tandem micro-pyrolysis-catalyst reactor system which separated the pyrolysis and catalytic stages. Fast pyrolysis conditions were used to process biomass (red oak) cellulose, hemicellulose and lignin with polyethylene plastic and the catalyst used was HZSM-5 zeolite. They reported strong synergistic interaction between the biomass and plastic both with and without the catalyst. Lignin interaction with the plastic was greater than with cellulose or hemicellulose, particularly producing enhanced yields of aromatic compounds. They concluded that the synergy between biomass and plastic occurs both during the pyrolysis stage and at the catalyst surface during the catalytic stage. It may be suggested that this is due to the fast pyrolysis conditions which facilitates interaction of the pyrolysis products and the separated catalyst stage which allows the pyrolysis product gases to interact at the zeolite catalyst sites. Kim et al [7] investigated the co-pyrolysis-catalysis of biomass (cellulose) and plastic (PP and low-LDPE (LLDPE)) in the presence of zeolite ZSM-5 and Y-zeolite catalysts representing different catalyst porosities. The reactors used were a TGA and a micro-pyrolyser GC-MS reactor, in each case the feedstock and catalysts were mixed together before co-pyrolysis. They reported that the effectiveness of the ZSM-5 and Y-zeolite catalysts were linked to their different porosities but also the molecular size of the co-pyrolysis reactants. Aromatic compound formation was easily achieved with the Y-zeolite for both LLDPE and PP because the larger molecular weight species could enter and react in the larger pores of the Y-zeolite catalyst.

Novel research by Dorado et al [34] used isotopic labelling of cellulose to determine the origin of the carbon contained in aromatic and alkene products produced from co-pyrolysis-catalysis of the cellulose (biomass) and different types of plastic (HDPE, LDPE, PET and PS). The catalyst used was HZSM-5 zeolite. They used a fast micro-pyrolysis reactor system at 650 °C involving a micro-pyrolyser coupled to a GC-MS analyser. The products were analysed by the GC-MS in terms of product composition, but also in terms of the distribution of $^{13}C_x$, from the isotopically labelled cellulose and $^{12}C_y$ from the non-labelled plastic. They reported that the aromatic hydrocarbon molecules produced from the catalytic fast pyrolysis of the cellulose and plastic mixtures in all cases contain carbon derived from both the biomass component and also the plastic component of the mixture. Additionally, they also reported that the products of co-pyrolysis-catalysis of the polyalkene plastics

(HDPE and LDPE) with cellulose favour the formation of alkylbenzenes while the aromatic plastics (PET and PS) with cellulose favour the formation of naphthalenes; as also reported in the work reported here.

Therefore, the literature suggests that the interaction of the biomass and the different plastics occurs during the first stage pyrolysis, particularly where the volatile biopolymer components devolatilise over a similar temperature regime to the devolatilisation of the plastics [23, 28]. There is also evidence that the biomass char may interact with the volatiles derived from plastics pyrolysis [29]. Subsequently, there is potential for interaction of the volatiles produced from pyrolysis of biomass and plastics over the zeolite ZSM-5 catalyst [14, 32, 33]. Using a two-stage co-pyrolysis catalysis system as used in this work, suggests interaction of biomass and plastics in the co-pyrolysis first stage and also the zeolite second stage catalysis is inevitable.

The used catalyst material after the pyrolysis-catalysis of the biomass and selected plastics and the co-pyrolysis-catalysis of biomass:plastic (1:1) mixtures was analysed by temperature programmed oxidation (TPO). Table 7 shows the results, representing the amount of catalyst carbon (coke) deposits. Biomass produced a catalyst carbon deposit of 3.1 wt.%, with the PET producing the highest coke deposit of 5.5 wt.%, significantly higher that the HDPE and PS. The mixture of biomass:HDPE produced a carbon deposit of 2.5 wt.% for the which is higher than expected by calculation of the individual biomass and HDPE (2.1 wt.%). The biomass:PS mixture produced a carbon deposit of 2.8 wt.%, also higher than the calculated deposit (2.5 wt.%). However, the mixture of biomass:PET produced a carbon deposit of 2.7 wt.%, which was lower than the expected calculated carbon deposit (4.3 wt.%).

### *3.3 Influence of biomass:plastic ratio on product gas and oil yield and composition*

High density polyethylene as a representative polyalkene structured plastic and polystyrene as a representative aromatic structured plastic were chosen to investigate the influence of different biomass:plastic ratios on the yield and composition of the product oils and gases from co-pyrolysis-catalysis of biomass and plastic. The ratios investigated were biomass:plastic ratios of 9:1, 4:1 and 1:1.

#### *3.3.1. Influence of biomass:high density polyethylene ratio*

Table 8 shows the co-pyrolysis-catalysis of different mixtures of biomass with high density polyethylene and also polystyrene in relation to product yield. The higher content of HDPE in the mixture (BMS:HDPE ratios 4:1 and 1:1) resulted in a decreased mass of char yield, reflected in the higher char yield produced from biomass pyrolysis. In relation to the liquid and gas yield at the higher HDPE contents, the general trend was an increase in both liquid and gas yield as a consequence of the lower char yield. Figure 5 shows that the composition of the product gases and shows that the increase in the content of plastic in the biomass:HDPE mixtures produces an increase in $C_nH_m$ hydrocarbons and an decrease in the CO and CO2 yield.

Table 9 shows the relative proportion of compounds, (normalised to 100% in each compound category), in the upgraded bio-oil from the co-pyrolysis-catalysis of the different ratios of biomass:HDPE. As before, the compositional categories used represented a semi-quantitative overview of the influence of different biomass:plastic ratios on bio-oil, and each category of compounds is not mutually exclusive. At the higher content of HDPE in the mixture, the relative proportion of oxygenated compounds in the product bio-oil was lower (11.7%). This was also reflected in the higher relative proportion of aliphatic structure containing compounds and lowered relative proportion of aromatic containing structured compounds as more plastic was contained in the biomass:HDPE mixture. Such compounds are derived from the complex biomass pyrolysis-catalysis derived oils.

### *3.3.2. Influence of biomass:polystyrene ratio*

Table 8 also shows the product yield from the co-pyrolysis-catalysis of different ratios of biomass with polystyrene. The influence of increased plastic content in the co-pyrolysis mixture produced lower char and gas yield and higher liquid yield. Figure 6 shows the composition of the product gases and shows a similar effect to that shown with biomass:HDPE in Figure 5, of an increase in $C_nH_m$ hydrocarbons and a decrease in the CO and $CO_2$ yield as the content of plastic in the biomass:plastic mixture was increased.

Table 10 shows the relative proportion of compounds, (normalised to 100% in each compound category), for the different categories of types of compounds found in the upgraded bio-oil from the co-pyrolysis-catalysis of the different ratios of biomass:polystyrene. The increased addition of polystyrene to the biomass:plastic mixture produces an oil with reduced oxygen content and a more aromatic product oil. The relative proportion of aromatic ring containing compounds, oxygen containing compounds, gasoline fuel range compounds and single-ring aromatic compounds which were identified all decreased as the plastic content was increased.

Kumar and Srinivas [35] investigated different ratios of biomass (ground nut shell) to plastic (PP and PS) for the production of upgraded bio-oil. They used a slow pyrolysis-catalytic fixed bed reactor where the catalyst in the form of spent FCC zeolite catalyst was mixed with the feedstock. Increasing the relative proportion of biomass in the biomass:PP mixture from 0.5:1 to 2:1, showed an increase in char yield and a decrease in gas and liquid yield, similar results to that of biomass:HDPE used in this work. Higher input of PP to the biomass also produced a product liquid with decreased content of oxygenated compounds and increased content of aliphatic alkenes. The trend in the content of aromatic compounds were less clear, with the lowest aromatic content at a biomass:PP ratio of 1:1, which was attributed to different reaction mechanisms for aromatics formation. However, increasing input of PP resulted in an increased content of individual aromatic compounds, particularly, xylene, alkylbenzene and polycyclic aromatic hydrocarbons and a decrease in oxygenated phenol. The results reported here also showed an decrease in the content of oxygenated compounds with increased addition of HDPE, but the range of the biomass:plastic ratio was much wider than Kumar and Srinivas [35]. They also reported on the influence of biomass:PS ratio on product yield and composition. Increased addition of polystyrene to the biomass produced a decrease in char and gas yield and increase in liquid yield, as also found in this work. They also showed that with higher addition of PS to the mixture, the content of oxygenated compounds in the product liquid were reduced. There was a high content of single-ring aromatic compounds, including styrene, ethylbenzene, styrene oligomers and benzene derivatives and polycyclic aromatic compounds in the product liquid at all of the biomass:PS ratios investigated.

## 4. Conclusions

In this work, the co-pyrolysis of biomass with several different waste plastics (HDPE, LDPE, PP, PET and PS) has been carried out and the product pyrolysis gases passed over zeolite ZSM-5 catalyst. The aim was to improve the quality of the product bio-oils. Overall, this work has shown that waste plastics can be added to biomass at the pyrolysis stage and with catalytic zeolite upgrading can produce a product bio-oil that is lower in the relative proportion of oxygenated compounds and with a high relative proportion of the hydrocarbons in the $C_5$ — $C_{12}$ carbon number fuel range. There was evidence of interaction between the plastics and biomass with increased yield of $C_nH_m$ hydrocarbons for co-pyrolysis-catalysis. However, any interaction during the co-pyrolysis stage will depend on the composition of the biomass and the particular plastic under investigation. This is due to the different thermal degradation profile and evolution of volatiles in relation to pyrolysis of the biomass including the components of biomass (cellulose, hemicellulose and lignin) and the thermal degradation profile and release of volatiles from the plastics.

The addition of the plastics to the biomass via co-pyrolysis-catalysis results in deoxygenation of the product bio-oils with increased aromatic compound content and lowered carbon number range. The addition of the polyalkene plastics (HDPE, LDPE, PP) to the biomass produced a upgraded bio-oil with the relative proportion of oxygenated compounds comprising 10.2% — 12.3%. The co-pyrolysis-catalysis of biomass and PS produced an upgraded product oil with a very low relative proportion of oxygenated compound content at 2.1%, whereas biomass:PET contained 19.7% oxygenated compounds reflecting the oxygen content of both the biomass and PET. Significant improvement in the deoxygenation of the upgraded bio-oils was also found with low inputs of plastic (9:1 biomass:plastic ratio), particularly with the addition of polystyrene to biomass.

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**Table 1.** Characteristics of the biomass and plastic wastes.

| | Biomass | HDPE | LDPE | PET | PP | PS |
|---|---|---|---|---|---|---|
| **Proximate analysis (wt.%)** | | | | | | |
| Moisture [a] | 7.8 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Ash [b] | 0.3 | 4.1 | 0.3 | 42.7 | 0.8 | 1.6 |
| Volatile [c] | 93.3 | 98.1 | 100.0 | 94.6 | 100.0 | 100.0 |
| Fixed Carbon [c] | 6.7 | 1.9 | 0.0 | 5.4 | 0.0 | 0.0 |
| **Elemental analysis (wt.%)** | | | | | | |
| C [c] | 50.1 | 82.5 | 83.3 | 69.0 | 81.0 | 87.8 |
| H [c] | 5.4 | 13.1 | 12.6 | 5.0 | 11.4 | 9.5 |
| O [c] | 48.6 | 1.8 | 0.7 | 32.7 | 0.6 | 0.0 |
| N [c] | 0.1 | 0.1 | 0.1 | 0.0 | 0.1 | 0.0 |

[a] as received; [b]dry; [c]dry ash-free

**Table 2.** Product yields for char, oil and gas from the pyrolysis-catalysis (zeolite ZSM-5) of biomass, biomass with sand as a blank catalyst material and from the pyrolysis-catalysis (zeolite ZSM-5) of waste plastic samples.

| | **Char (wt.%)** | **Liquid (wt.%)** | **Gas (wt.%)** |
|---|---|---|---|
| Biomass Blank (Sand) | 25.1 | 56.3 | 15.6 |
| Biomass - ZSM-5 | 25.6 | 49.3 | 27.1 |
| LDPE - ZSM-5 | 0.0 | 72.5 | 30.9 |
| HDPE - ZSM-5 | 6.6 | 64.3 | 37.2 |
| PP - ZSM-5 | 0.5 | 75.1 | 31.6 |
| PET - ZSM-5 | 39.6 | 38.1 | 24.4 |
| PS - ZSM-5 | 1.4 | 86.4 | 16.4 |

**Table 3.** Relative proportion of compounds, (normalised to 100% in each compound category), in plastic derived pyrolysis oil which were aromatic, oxygenated or in the fuel range $C_5$ — $C_{12}$ or 1-4 ring aromatic/linear aliphatic for oil derived from the pyrolysis-catalysis of the waste biomass and plastics with ZSM-5 catalyst. Presented as total ion chromatogram percentage peak area.

| | **Sand** | **BMS** | **LDPE** | **HDPE** | **PP** | **PET** | **PS** |
|---|---|---|---|---|---|---|---|
| Aromatic ring containing compounds (%) | 64.4 | 94.4 | 28.7 | 37.0 | 33.0 | 100.0 | 100.0 |
| Aliphatic containing compounds (%) | 35.6 | 0.6 | 71.3 | 63.0 | 67.0 | 0.0 | 0.0 |
| Oxygenated compounds (%) | 99.8 | 37.3 | 0.0 | 0.6 | 0.6 | 11.0 | 0.0 |
| Non-oxygenated (%) | 0.2 | 62.7 | 100.0 | 99.4 | 99.4 | 89.0 | 100.0 |
| $C_5$ — $C_{12}$ (%) | 98.2 | 97.2 | 49.1 | 55.4 | 67.2 | 96.5 | 76.3 |
| $\geq C_{13}$ (%) | 1.8 | 2.8 | 50.9 | 44.6 | 32.8 | 3.5 | 23.7 |
| Single-ring aromatic (%) | 88.9 | 83.6 | 34.4 | 41.2 | 42.7 | 61.9 | 57.0 |
| Two-ring aromatic (%) | 0.7 | 13.6 | 0.4 | 0.3 | 0.3 | 34.6 | 32.1 |
| Three-ring aromatic (%) | 0.0 | 2.7 | 0.0 | 0.0 | 0.1 | 3.4 | 5.5 |
| Four-ring aromatic (%) | 0.0 | 0.1 | 0.0 | 0.0 | 0.1 | 0.1 | 5.5 |
| Linear aliphatic (%) | 10.4 | 0.0 | 65.1 | 58.5 | 56.8 | 0.0 | 0.0 |

**Table 4.** Product yields for char, oil and gas from the pyrolysis-catalysis (zeolite ZSM-5) of mixed biomass and waste plastics (1:1).

| | **Char (wt.%)** | **Liquid (wt.%)** | **Gas (wt.%)** |
|---|---|---|---|
| BMS:LDPE | 13.1 | 56.0 | 36.6 |
| BMS:HDPE | 15.0 | 53.1 | 31.4 |
| BMS:PP | 15.1 | 51.6 | 35.9 |
| BMS:PET | 37.9 | 37.9 | 22.2 |
| BMS:PS | 16.3 | 66.3 | 18.9 |

**Table 5:** Calculated product yields for char, oil and gas based on the predicted 1:1 ratio of co-pyrolysis-catalysis yields from Table 2.

| | Char (wt.%) | Liquid (wt.%) | Gas (wt.%) |
|---|---|---|---|
| BMS:LDPE | 12.8 | 61.0 | 29.1 |
| BMS:HDPE | 16.1 | 56.9 | 32.2 |
| BMS:PP | 13.0 | 62.3 | 29.4 |
| BMS:PET | 32.6 | 43.8 | 25.8 |
| BMS:PS | 13.5 | 67.9 | 21.8 |

**Table 6.** Relative proportion of compounds, (normalised to 100% in each compound category), in plastic and biomass derived co-pyrolysis oil which were aromatic, oxygenated, in the fuel range ($C_5$ — $C_{12}$) or 1-4 ring aromatic/linear aliphatic. Presented as total ion chromatogram percentage peak area.

| | **BMS:LDPE** | **BMS:HDPE** | **BMS:PP** | **BMS:PET** | **BMS:PS** |
|---|---|---|---|---|---|
| Aromatic ring containing compounds (%) | 52.5 | 42.1 | 43.1 | 100.0 | 95.6 |
| Aliphatic containing compounds (%) | 47.5 | 57.9 | 56.9 | 0.0 | 4.4 |
| Oxygenated compounds (%) | 12.3 | 11.7 | 10.2 | 19.7 | 2.1 |
| Non-oxygenated compounds (%) | 87.7 | 88.3 | 89.8 | 80.3 | 97.9 |
| $C_5$ — $C_{12}$ (%) | 66.2 | 51.8 | 72.1 | 89.1 | 75.7 |
| $\geq C_{13}$ (%) | 33.8 | 48.2 | 27.9 | 10.8 | 24.3 |
| Single-ring aromatic (%) | 49.4 | 40.4 | 49.3 | 65.7 | 62.2 |
| Two-ring aromatic (%) | 3.1 | 1.7 | 0.8 | 27.1 | 24.6 |
| Three-ring aromatic (%) | 0.0 | 0.0 | 0.0 | 7.1 | 6.1 |
| Four-ring aromatic (%) | 0.0 | 0.0 | 0.0 | 0.1 | 2.8 |
| Linear aliphatic (%) | 47.5 | 57.9 | 49.9 | 0.0 | 4.4 |

**Table 7.** Amount of carbon deposits on the used ZSM-5 catalysts after pyrolysis-catalysis of the biomass, plastics and the biomass:plastic mixtures determined by temperature programmed oxidation.

| **Feedstock** | **Carbon deposits (wt.%)** |
|---|---|
| Biomass (BMS) | 3.1 |
| HDPE | 1.1 |
| PET | 5.5 |
| PS | 1.9 |
| BMS:HDPE | 2.5 |
| BMS:PET | 2.7 |
| BMS:PS | 2.8 |

**Table 8.** Product yields for the co-pyrolysis-catalysis of biomass:HDPE at different mixing ratios.

| | **Char (wt.%)** | **Liquid (wt.%)** | **Gas (wt.%)** |
|---|---|---|---|
| BMS:HDPE (9:1) | 23.0 | 51.5 | 29.0 |
| BMS:HDPE (4:1) | 21.1 | 48.7 | 33.7 |
| BMS:HDPE (1:1) | 15.0 | 53.1 | 31.4 |
| BMS:PS (9:1) | 24.5 | 52.6 | 28.6 |
| BMS:PS (4:1) | 22.0 | 59.5 | 22.3 |
| BMS:PS (1:1) | 16.3 | 66.3 | 18.9 |

**Table 9.** Relative proportion of compounds, (normalised to 100% in each compound category), in product oils which were aromatic, oxygenated, in the fuel range $C_5$-$C_{12}$ or 1-4 ring aromatic/linear aliphatic for oil derived from the pyrolysis-catalysis of the waste biomass and HDPE with ZSM-5 catalyst with different mixtures of biomass and HDPE. Presented as total ion chromatogram percentage peak area.

| | **BMS:HDPE (9:1)** | **BMS:HDPE (4:1)** | **BMS:HDPE (1:1)** |
|---|---|---|---|
| Aromatic ring containing compounds (%) | 88.5 | 77.6 | 42.1 |
| Aliphatic containing compounds (%) | 11.5 | 22.4 | 57.9 |
| Oxygenated (%) | 15.2 | 11.6 | 11.7 |
| Non-oxygenated (%) | 84.8 | 88.4 | 88.3 |
| $C_5$ — $C_{12}$ (%) | 88.7 | 85.8 | 51.8 |
| $\geq C_{13}$ (%) | 11.3 | 14.2 | 48.2 |
| Single-ring aromatic (%) | 72.0 | 66.8 | 40.4 |
| Two-ring aromatic (%) | 15.8 | 10.7 | 1.7 |
| Three-ring aromatic (%) | 0.7 | 0.0 | 0.0 |
| Four-ring aromatic (%) | 0.0 | 0.0 | 0.0 |
| Linear aliphatic (%) | 11.5 | 22.4 | 57.9 |

**Table 10.** Relative proportion of compounds, (normalised to 100% in each compound category), in product oils which were aromatic, oxygenated, in the fuel range $C_5$-$C_{12}$ or 1-4 ring aromatic/linear aliphatic for oil derived from the pyrolysis-catalysis of the waste biomass and PS with ZSM-5 catalyst with different mixtures of biomass and PS. Presented as total ion chromatogram percentage peak area.

| | **BMS:PS (9:1)** | **BMS:PS (4:1)** | **BMS:PS (1:1)** |
|---|---|---|---|
| Aromatic ring containing compounds (%) | 100.0 | 100.0 | 95.6 |
| Aliphatic containing compounds (%) | 0.0 | 0.0 | 4.4 |
| Oxygenated (%) | 16.9 | 12.6 | 2.1 |
| Non-oxygenated (%) | 83.1 | 87.4 | 97.9 |
| $C_5$ — $C_{12}$ (%) | 91.2 | 82.9 | 75.7 |
| $\geq C_{13}$ (%) | 8.8 | 17.1 | 24.3 |
| Single-ring aromatic (%) | 78.5 | 64.6 | 62.2 |
| Two-ring aromatic (%) | 19.7 | 27.2 | 24.6 |
| Three-ring aromatic (%) | 1.4 | 6.5 | 6.1 |
| Four-ring aromatic (%) | 0.5 | 1.7 | 2.8 |
| Linear aliphatic (%) | 0.0 | 0.0 | 4.4 |

## Figure Captions

**Figure  1.** Schematic diagram of the pyrolysis-catalysis reactor system

**Figure 2.** Gas composition from the pyrolysis-catalysis of waste biomass for ZSM-5 zeolite catalyst in comparison with quartz sand in the 2nd stage catalytic reactor

**Figure 3**. Gas composition from the pyrolysis-catalysis of plastics with ZSM-5 catalyst.

**Figure 4**. Gas composition from the pyrolysis-catalysis of biomass:plastic mixtures (1:1) with ZSM-5 catalyst.

**Figure 5**. Gas composition from the pyrolysis-catalysis of biomass:HDPE with ZSM-5 catalyst in relation to different biomass:HDPE ratios.

**Figure 6**. Gas composition from the pyrolysis-catalysis of biomass:PS with ZSM-5 catalyst in relation to different biomass:PS ratios.

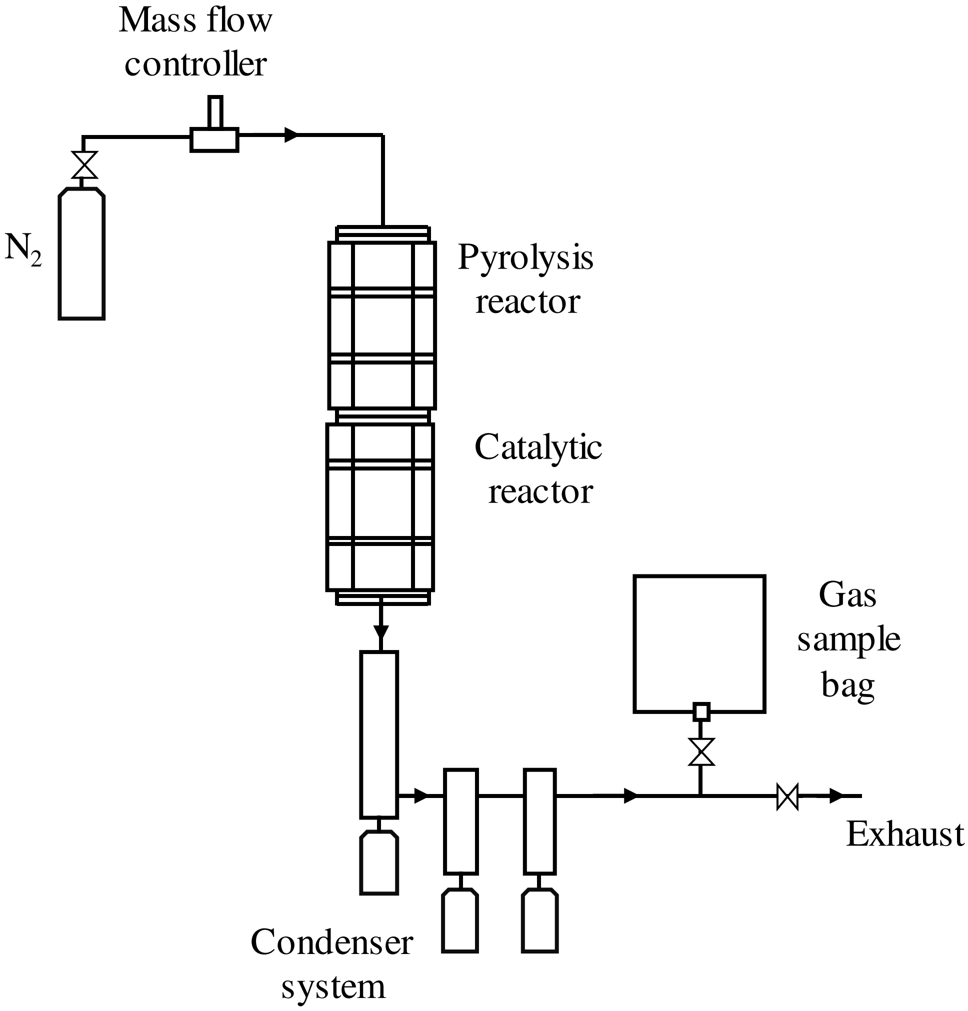

**Figure 1.** Schematic diagram of the pyrolysis-catalytic reactor system

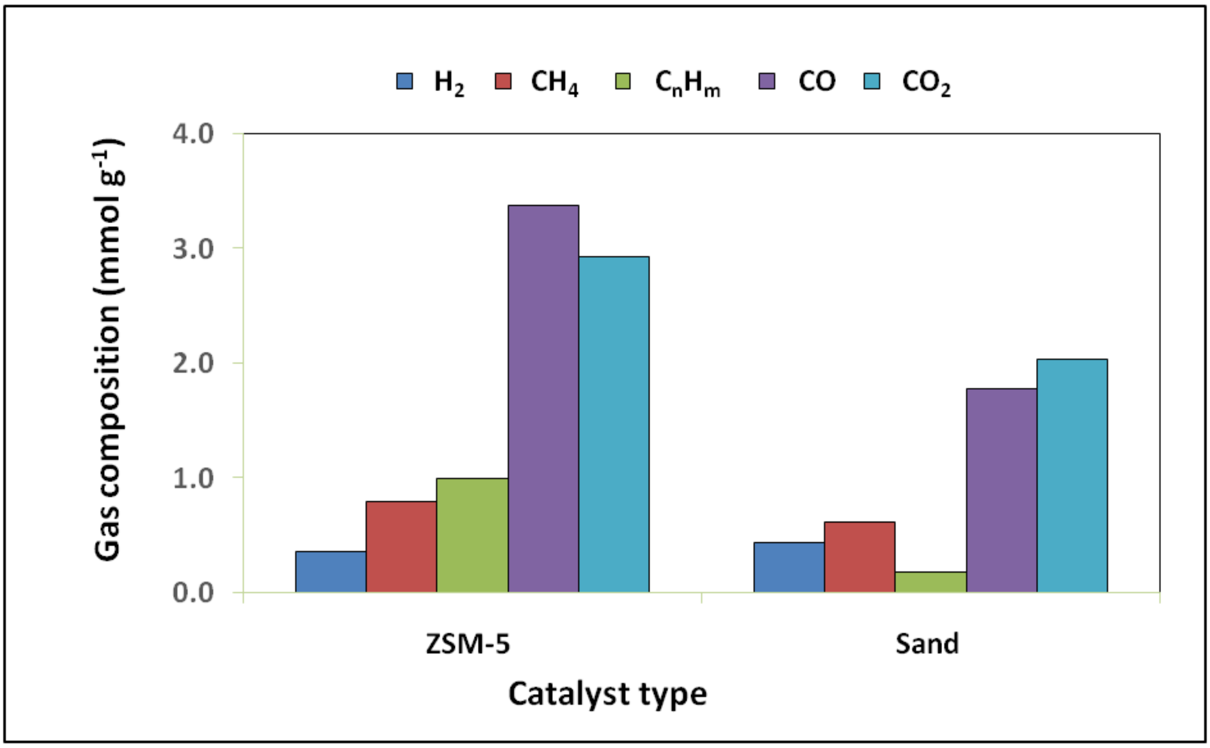

**Figure 2.** Gas composition from the pyrolysis-catalysis of waste biomass for ZSM-5 zeolite catalyst in comparison with quartz sand in the 2nd stage catalytic reactor

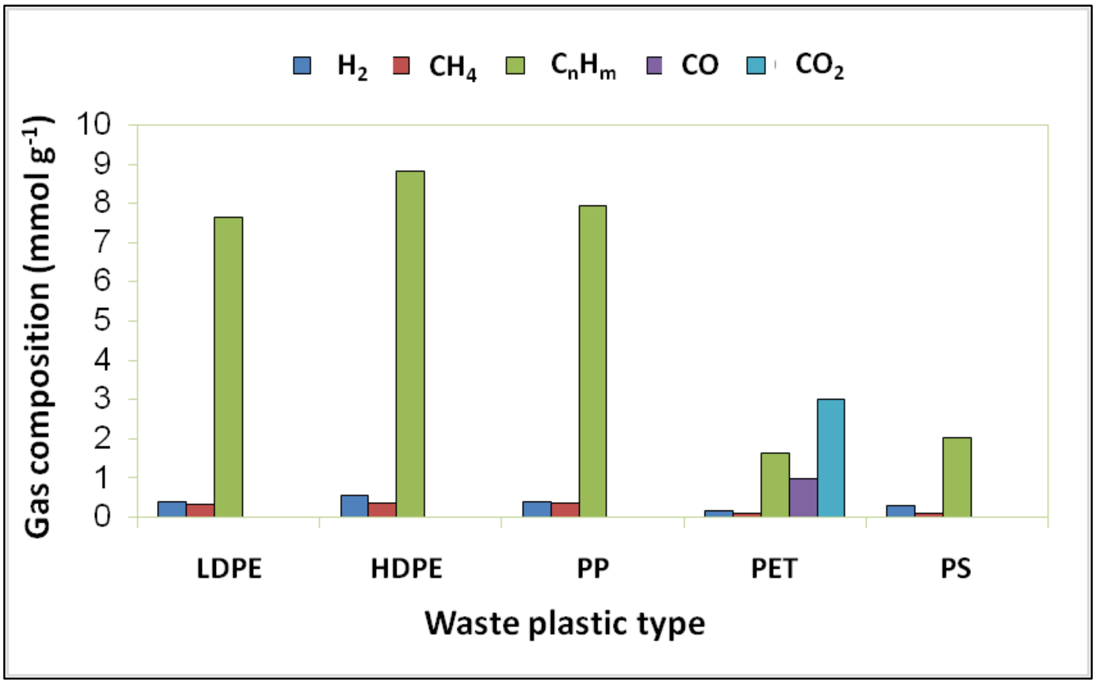

**Figure 3**. Gas composition from the pyrolysis-catalysis of plastics with ZSM-5 catalyst.

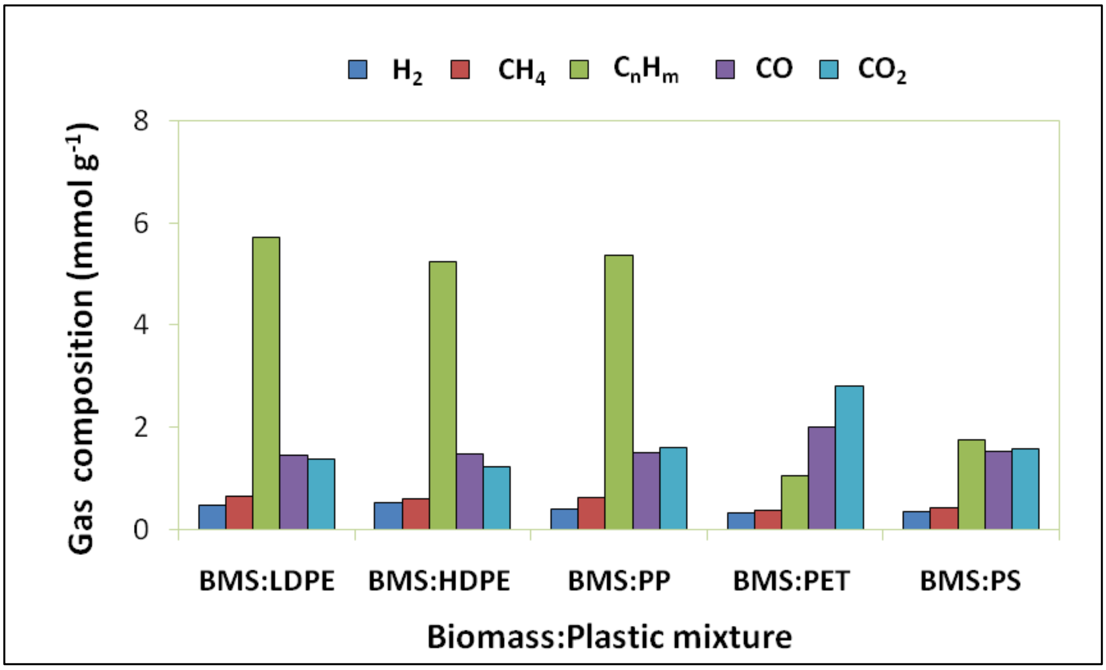

**Figure 4**. Gas composition from the pyrolysis-catalysis of biomass:plastic mixtures(1:1) with ZSM-5 catalyst.

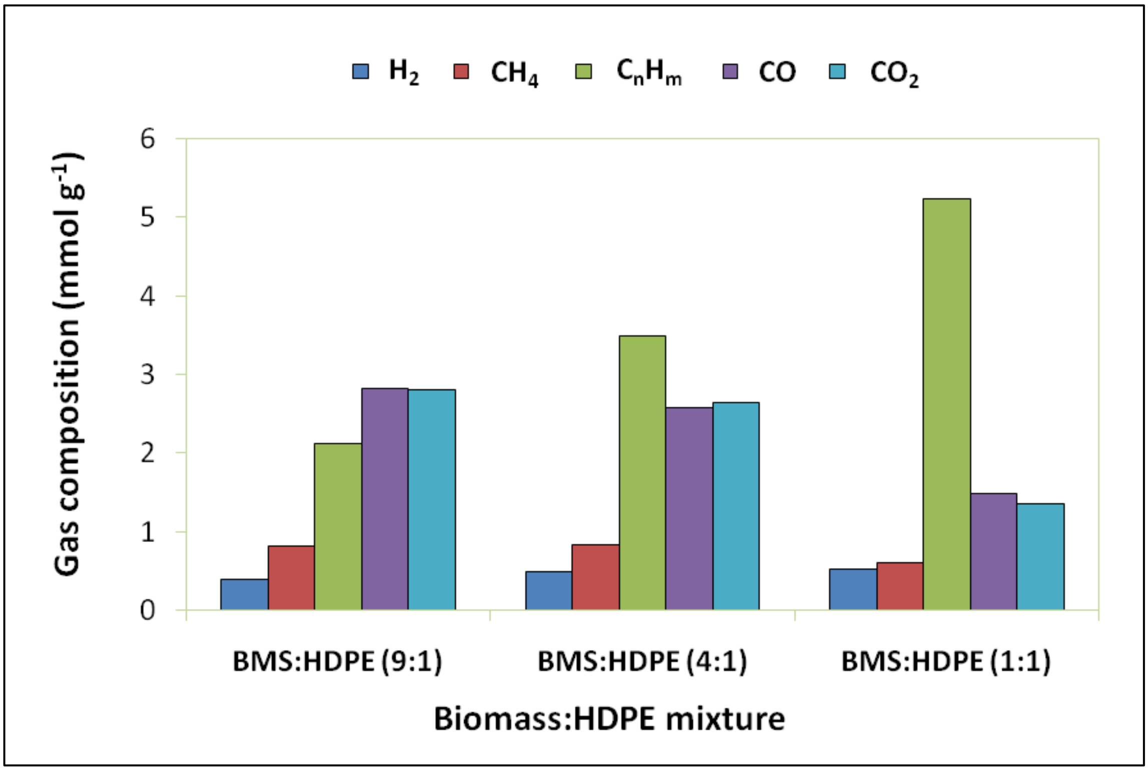

**Figure 5**. Gas composition from the pyrolysis-catalysis of biomass:HDPE with ZSM-5 catalyst in relation to different biomass:HDPE ratios.

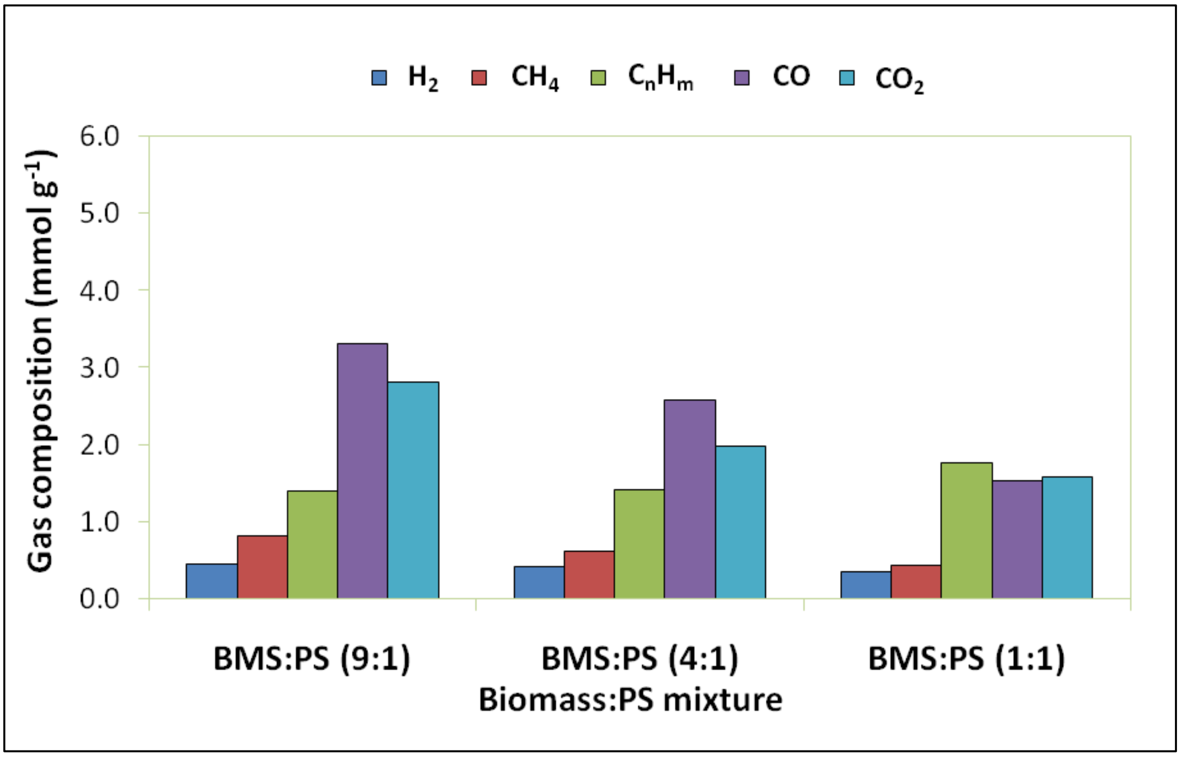

**Figure 6**. Gas composition from the pyrolysis-catalysis of biomass:PS with ZSM-5 catalyst in relation to different biomass:PS ratios.