



# Carbon nanotubes and hydrogen production from the pyrolysis catalysis or catalytic-steam reforming of waste tyres



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## ABSTRACT

A range of process conditions have been investigated to maximise the production of carbon nanotubes (CNTs) and/or hydrogen from waste tyres. A two-stage pyrolysis-catalytic reactor system was used and the influence of catalyst temperature (700, 800 and 900 °C), tyre: catalyst ratio (1:0.5, 1:1 and 1:2) and steam input (water injection 0, 2 and 5 ml h<sup>-1</sup>) to the second catalyst stage were investigated. The catalyst used was a Ni/Al<sub>2</sub>O<sub>3</sub> catalyst prepared by a wetness impregnation technique. Carbon was deposited on the catalyst surface during pyrolysis-catalysis increasing with increasing catalyst temperature and also increasing as the tyre: catalyst ratio was raised. Examination of the carbon showed it to be composed of largely filamentous type carbons, producing 253.7 mg g<sup>-1</sup> tyre of filamentous carbons at a tyre: catalyst ratio of 1:1 and catalyst temperature of 900 °C. A significant proportion of the deposited filamentous carbons were multi-walled carbon nanotubes as shown by transmission electron microscopy characterisation. The introduction of steam to the process enhanced hydrogen production, producing a maximum of 34.69 mmol g<sup>-1</sup> tyre at a water injection rate of 5 ml h<sup>-1</sup>.

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## 1. Introduction

With the demand for automobiles growing globally each year, the environmental issues caused by waste tyre disposal have become more serious [1]. Waste tyres are a mixture of elastomers (e.g. natural rubber, butadiene and styrene-butadiene rubbers), carbon black filler/strengthener, metal reinforcements and zinc, sulphur and other additives [2]. The approaches to manage the waste tyre issue include energy recovery recycling and reuse. In Europe, around 33 wt.% of waste tyres are estimated to be recovered as an alternative material in civil engineering applications, 35 wt.% of waste tyre is recovered as an alternative fuel for energy recovery in cement kilns, 8 wt.% of waste tyre contributes to re-treading and 10 wt.% to export [3].

The typical tyre has a high carbon content at ~81.2 wt.% and hydrogen content ~7.2 wt.% [4]. The recovery of valuable products from tyres has been studied by many researchers, including the production of hydrogen, aromatic chemicals, activated carbon etc. [3–6]. Pyrolysis as a thermal degradation process to recover more valuable products from waste tyre has been investigated as a process option [3,6]. The typical pyrolysis temperature is ~500 °C,

where the waste tyre is heated in an inert atmosphere to produce waste tyre degradation products including gases, solid carbon and liquid oil [3]. The gaseous products contain hydrogen and C<sub>1</sub>–C<sub>4</sub> hydrocarbons and have a high calorific value of up to 65 MJ m<sup>-3</sup> depending on process conditions [3]. During gasification of waste tyre, hydrogen-enriched syngas is normally the target product; the syngas can be used for power generation using internal combustion gas engines or for producing chemicals through the Fischer-Tropsch process [7–10]. Hydrogen is regarded as a clean energy carrier for a projected future hydrogen economy, as it can be produced from many sources and its combustion only generates water and also has broad applications such as use in fuel cells [11]. Catalysts are normally used to improve the efficiency of hydrogen production from the pyrolysis-reforming of waste tyres. For example, Elbaba et al. [7,12–14] investigated several nickel based catalysts to improve the production of hydrogen. They used a two-stage pyrolysis coupled catalytic steam reforming using nickel catalysts to produce a syngas with high a high content of hydrogen (65 vol.%) from waste tyres [14]. They also reported that higher nickel contents in the catalyst and increased temperature and steam input produced higher levels of hydrogen [7,12].

However, due to the catalyst deactivation caused by coke formation on the surface of catalyst [15], the waste tyre conversion efficiency could thereby decrease significantly [16,17]. But, recent work [18] by the authors has shown that under some process con-

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ditions, the carbon deposited on the catalyst surface is composed of significant amounts of carbon nanotubes. Carbon nanotubes (CNTs) have a high potential impact in many industrial applications due to their special physical and chemical properties. For example, CNTs can be applied as multifunctional coating materials, where multi-walled carbon nanotubes (MWCNTs) can be additives in paint production which aims to reduce bio-fouling [19,20]. The life cycle of batteries or capacitors can be extended with the addition of MWCNTs due to increased electronic connectivity and mechanical integrity [19,21,22]. Considering the chemical and dimensional compatibility of CNTs with biomolecules, they have also been used in biosensors and medical devices [19,23].

The most common method to synthesis CNTs is via a chemical vapour deposition (CVD) process from hydrocarbons such as methane, benzene, xylene or other hydrocarbons [24,25]. However, the hydrocarbons generated from the pyrolysis of waste tyres contain more than 100 hydrocarbon species [3]. For example, the gas phase produced from pyrolysis of tyres alkanes and alkene hydrocarbon gases from C<sub>1</sub>–C<sub>4</sub>. Higher molecular weight hydrocarbons will also be generated during pyrolysis of the tyres. The condensed oil fraction from pyrolysis of waste tyres have been shown to be a wide range of hydrocarbon species, including aliphatic, aromatic, hetero-atom and polar hydrocarbons. For example, alkanes from C<sub>10</sub>–C<sub>35</sub>, alkenes from C<sub>6</sub>–C<sub>9</sub>, single ring aromatic compounds such as benzene, toluene, xylene (BTX), styrene and alkylated derivatives, polycyclic aromatic hydrocarbons such as naphthalene, biphenyl, phenanthrene, anthracene, pyrene and alkylated derivatives and a wide range of other hydrocarbons including phenols, organic acids and sulphur and nitrogen containing hydrocarbons [3]. Therefore, waste tyres, with their high content of hydrocarbons also represent a potential feedstock for the production of CNTs through a pyrolysis process that generates a wide range of hydrocarbon species. Yang et al. [26] successfully used waste tyres as an alternative carbon source to produce CNTs by a CVD method over a cobalt based catalyst. Co-producing of hydrogen and CNTs from waste tyre by pyrolysis catalysis was also investigated in our previous studies [4,18]. Different catalysts (Co/Al<sub>2</sub>O<sub>3</sub>, Cu/Al<sub>2</sub>O<sub>3</sub>, Ni/Al<sub>2</sub>O<sub>3</sub>, Fe/Al<sub>2</sub>O<sub>3</sub>) were investigated to determine the catalyst for optimized hydrogen and CNTs production by a pyrolysis-catalysis process [18]; the different types of waste tyre and typical elastomers used in tyre formulation (natural rubber, butadiene and styrene-butadiene rubbers) were also investigated to better understand the pyrolysis-catalysis process for both hydrogen and CNTs production [4].

It is interesting to develop a process that can produce both hydrogen and carbon nanotubes from waste materials such as waste tyres. The process has the flexibility to produce either hydrogen or carbon nanotubes by altering the process conditions. In this paper, different experimental process conditions including water injection rate, catalysis temperature and tyre to catalyst ratio were investigated, with the aim of improving hydrogen and multi-walled carbon nanotubes (MWCNTs) production from waste tyres by pyrolysis catalysis or catalytic-reforming processes.

## 2. Materials and methods

### 2.1. Materials

The waste tyre sample was obtained from truck tyres with metal and reinforcing fabric removed and the remaining rubber shredded to produce rubber particles of size ~6 mm. The waste tyre sample contained ~81.16 wt.% of carbon, ~7.17 wt.% hydrogen and metals [4]. The Ni/Al<sub>2</sub>O<sub>3</sub> catalyst was synthesised by a wetness impregnation method with 10 wt.% nickel loading. Nickel nitrate which was the nickel precursor was dissolved into ethanol; the alumina sup-

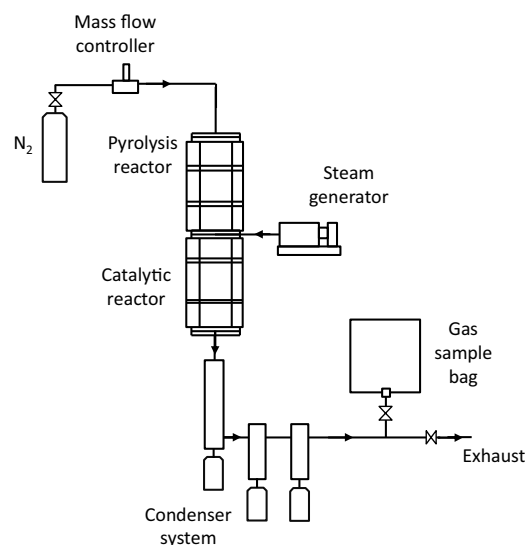


Fig. 1. Schematic diagram of the two stage fixed-bed pyrolysis catalytic-reforming reactor system.

port (obtained from Sigma Aldrich, UK) was added into the nickel nitrate and ethanol solution to produce a slurry under continuous stirring; the slurry was dried overnight at 90 °C in an oven; the solid product was calcined in an oven with a 2 °C min<sup>-1</sup> heating rate to a final temperature of 750 °C with 3 h holding time; finally, the catalyst was crushed and sieved to obtain the catalyst as granules of size in a range of 0.05–0.18 mm. The same procedure, preparation and characterisation of the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst has been reported previously [18]. Reduction of the catalyst occurred *in-situ* by the generated process gases, particularly hydrogen and carbon monoxide [27].

### 2.2. Experimental system

A two stage fixed-bed reactor as shown in Fig. 1 was used to conduct the tyre pyrolysis-catalysis/catalytic-reforming experiments. Pyrolysis-catalysis experiments did not use the steam injection system and investigated the influence of catalyst temperature and tyre: catalyst ratio targeted at the increased production of catalyst carbon deposition coupled with carbon nanotube formation. Pyrolysis-catalytic steam reforming experiments involved the input of steam (water injection via a syringe pump) and investigated the influence of steam input rate targeted at the production of increased levels of hydrogen. The two stages of the reactor system consisted of a first stage pyrolysis of the tyres and a second stage containing the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst. The reactors were constructed of stainless steel and were separately externally electrically heated and temperature controlled. Three sets of experiments were conducted; the influence of different water injection rates at 0, 2 and 5 ml h<sup>-1</sup> on hydrogen production; the influence of catalyst temperatures of 700, 800 and 900 °C, and tyre: catalyst ratios at 1:0.5, 1:1 and 1:2 on the production of catalyst carbon. The waste tyre sample (1 g) was placed in a sample crucible in the pyrolysis stage and heated from ambient temperature to 600 °C at 40 °C min<sup>-1</sup>. The evolved volatiles from waste tyre pyrolysis passed directly through the catalytic reactor which was maintained at the desired catalyst temperature and where the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst was located. The reactor system was purged continuously with nitrogen gas to maintain inert conditions and as a carrier gas to purge gaseous products into the condensation system. The condensable liquids were collected in the condensers which were cooled by dry ice followed by collection of gases in a 25 L Tedlar™ gas sample bag for gas chromatography

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