
CARBON NANOTUBES AND HYDROGEN FROM PYROLYSIS-GASIFICATION OF WASTE PLASTICS

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Abstract

The production of hydrogen and carbon nanotubes (CNTs) from different plastics in a two stage pyrolysis-gasification reactor has been investigated in relation to process conditions. CNTs grew on the nickel catalyst and were analysed by electron microscopy, thermogravimetric analysis and Raman spectroscopy. One of the key process parameters was the introduction of steam which proved significant in the production of hydrogen with a rise observed at higher steam injection rates as steam reforming reactions increase. CNTs were produced from low density polyethylene, polypropylene and polystyrene; however it was found that the addition of water influenced the growth of CNTs differently depending on the plastic source. The largest CNT yield was obtained for polystyrene at a steam injection rate of 0.25 g/hr, and gave a conversion rate to CNTs of 29% wt. The CNTs produced were multiwalled CNTs and had a diameter of around 15nm. By simply changing the rate of steam injected the major product produced from the plastics can be shifted between CNTs and hydrogen, giving the potential for an industrial process which has great flexibility over its production.

Keywords: Carbon nanotubes, hydrogen, pyrolysis, gasification, plastics

1. Introduction

Carbon nanotubes (CNTs) are a material that have generated a great deal of scientific interest over recent years as a result of their remarkable properties, including a high strength, a large surface area and good electrical conductivity. The potential to produce them from a waste source such as waste plastics holds the opportunity to simultaneously tackle waste management issues and provide a cheap source of CNTs. Plastics pose a serious waste management problem since they make up a significant proportion of municipal solid waste, up to 10% by weight in England [1] but have a low recycling rate, only 25% in Europe [2].

Whilst a number of studies have produced CNTs from plastics before [3-7], to our knowledge this is the first study that has investigated the addition of steam to increase the yield of CNTs from a plastic feedstock. The use of steam for CNT production with an acetylene feedstock was investigated by Hata et al [8]. The injection of steam was found to be beneficial to the production of CNTs since reacts with amorphous carbons which deactivate the catalyst and prevent further CNT growth. This allowed larger yield and a higher purity of CNTs to be produced. This study aims to investigate the effect of different steam injection rates on the production of CNTs and hydrogen from various plastic sources.

2. Materials and Methods

Three different plastics were investigated for their ability to produce hydrogen and CNTs; low density polyethylene, polypropylene and polystyrene. The catalyst used was Ni-Al₂O₃ prepared by impregnation, with a nickel loading of 5%.

The experimental procedure was conducted in a two stage pyrolysis-gasification reactor. Plastics were pyrolysed in nitrogen at 600°C, before the evolved gases were passed to a second stage where steam was injected and the gases were heated at 800°C in the presence of a nickel-alumina catalyst. Carbon deposition in the form of CNTs would then occur on the surface of the catalyst. Experiments were conducted without steam injection and at injection rates between 0.25 g/hr and 4.74 g/hr. The volatile products after the gasification process were passed through two condensers, where any condensed products were collected. The non-condensed gases were collected in a 25 L Tedlar™ gas sample bag.

Gases were analysed by gas chromatography whilst the CNTs grown on the surface of the catalyst were analysed by scanning electron microscopy (SEM), transmission electron microscopy (TEM), temperature programmed oxidation and Raman spectroscopy.

3. Results and Discussion

The introduction and variation of steam had a profound effect on the production of hydrogen. As can be seen in figure 1 the yield was fairly low when no steam was added, however the addition of steam increased this, with further increases seen as the steam injection rate was raised. This was most likely due to an increase in steam reforming reactions and the reaction of steam with amorphous carbons.

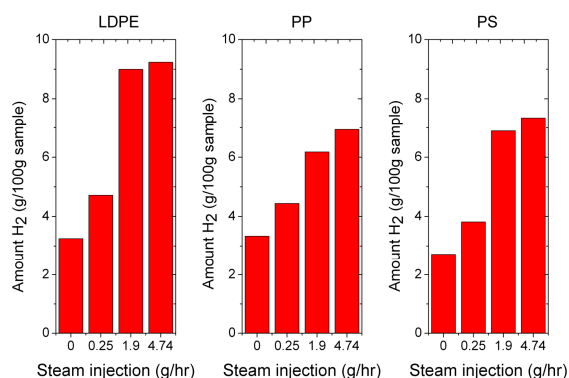


Figure 1: Hydrogen production from LDPE, PP and PS

CNTs were produced from all the plastic samples, with typical SEM and TEM images of the nanotubes produced shown in figures 2 and 3. From the SEM image in figure 2 it can be seen that a small amount of amorphous carbons and a large amount of long thin filament type carbons are present. The long thin deposits were thought to be CNTs, and this was confirmed with the use of TEM. As shown in figure 3, multi-walled carbon nanotubes with a diameter of around 15nm were observed.

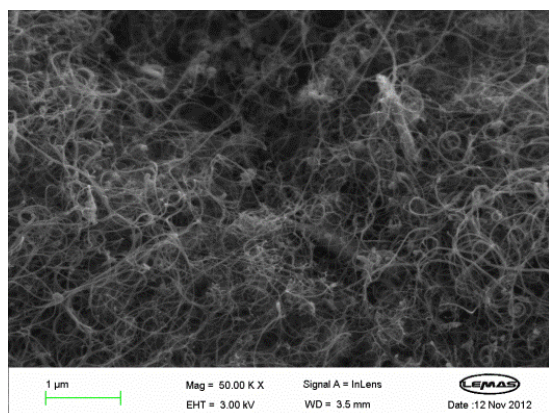


Figure 2: SEM image of carbon deposits on nickel catalyst

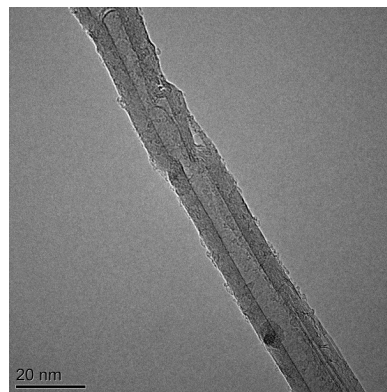


Figure 3: TEM image of CNT from plastic source

Temperature programmed oxidation was also used to determine the amount of CNTs that were produced. From the derivative plot different peaks were observed for amorphous and nanotubular carbons, and so the weight associated with the CNTs produced could be calculated. It was observed that increasing the steam injection rate affected each plastic differently in terms of producing CNTs. The largest CNT yield was obtained for polystyrene with a steam injection rate of 0.25 g/hr, with 29% of the plastic sample converted into nanotubes.

4. Conclusions

CNTs and hydrogen were successfully synthesized from three different plastic feedstocks, showing a range of plastic sources can be used to produce CNTs. Overall it was seen that the steam injection rate had a strong influence on production of both CNTs and hydrogen. As a result the process can be tailored to maximize either the production of hydrogen or CNTs from plastic sources. To optimize either the production of hydrogen or CNTs, the rate of steam injection simply needs altering, giving the potential for good flexibility as an industrial process.

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