Proceedings Paper:

Williams, PT, Wang, M, Miskolczi, N et al. (3 more authors) (2015) Flexi-pyrocat: A EU Marie Sklodowska-Curie action project on the flexible pyrolysis-catalysis processing of waste plastics for selective production of high value products. In: UNSPECIFIED 8th International Symposium on Feedstock Recycling of Polymeric Materials,, 7-10 September 2015, Leoben, Austria. .

FLEXI-PYROCAT: A EU MARIE SKŁODOWSKA-CURIE ACTION PROJECT ON THE FLEXIBLE PYROLYSIS-CATALYSIS PROCESSING OF WASTE PLASTICS FOR SELECTIVE PRODUCTION OF HIGH VALUE PRODUCTS

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Abstract

A recent EU Marie Skłodowska-Curie Action project, FLEXI-PYROCAT, has been awarded to develop a two-stage pyrolysis-catalytic process that allows flexible processing of waste plastics to selectively target and produce high value products - (i) hydrogen, (ii) carbon nanotubes, (iii) chemicals or (iv) gasoline. The project supports staff exchanges of experienced and early career researchers between the EU partner Universities in the UK and Hungary with world leading universities in China and Australia.

Pyrolysis technologies are not suitable for all types of wastes. However, the introduction of catalysts into the process can play a critical role in the thermochemical processing of waste plastics in terms of promoting targeted reactions, reducing reaction temperature and improving whole process efficiency. Technology which combines a first stage pyrolysis where the plastics are thermally degraded to produce volatile products which are then passed directly to a second separate catalytic stage has enormous potential; by careful selection of the correct catalyst and the catalytic process conditions the plant operator can then direct the process towards a flexible range of high value products.

Keywords: *Plastics; Hydrogen; Carbon nanotubes; Chemicals; Gasoline*

1. Introduction

More than 25 million tonnes of waste plastic are generated in the European Union each year [1]. Waste plastics have the potential for high levels of recycling, however, the overall recycling of plastics remains at a low level. Therefore, there is an urgent need to develop waste plastics recycling processes which are innovative, environmentally and socially acceptable with the potential for high economic reward. Pyrolysis is the thermal degradation of organic waste in the absence of oxygen to produce a carbonaceous char, oil and combustible gases. The oils may be used directly in fuel applications, the solid char can be used as a solid fuel and the gases generated contain sufficient energy for the energy requirements of a pyrolysis plant. Also, it is known that the process conditions of pyrolysis can alter the proportions of gas, solid and liquid products. Pyrolysis technology has been known for many years. However, the wide range of process technologies have resulted in many different small scale processes and no market leading technology. In addition, the vast majority of pyrolysis technologies under development are in general targeting low value products such as fuel oil with low throughputs. However, if plastic waste could be used to generate high value products, the economic viability of pyrolysis would be significantly increased.

Catalysts can play a critical role in the thermochemical processing of wastes in terms of promoting targeted reactions, reducing reaction temperature and improving whole process efficiency. Catalysts, have great potential for the pyrolysis-catalytic processing of plastic wastes but there are challenges in their successful development and deployment into an integrated pyrolysis-catalysis system.

The European Commission has awarded a Marie Skłodowska-Curie Action grant “FLEXI-PYROCAT”, to investigate an innovative two-stage pyrolysis-catalytic process that allows flexible processing of waste plastics to selectively target and produce high value products - (i) hydrogen, (ii) carbon nanotubes, (iii) chemicals or (iv) gasoline. The project involves a series of staff exchanges over a four year period between EU universities and and world-leading universities in China and Australia. The consortium of Universities involves the University of Leeds (UK) (Coordinator) the University of Hull (UK) the University of Pannonia, (Hungary) together with overseas universities in China, (University of Tsinghua and Huazhong University of Science and Technology) and Australia (University of Sydney). The EU project supports 140 man months of staff exchanges over 4 years to enhance knowledge interchange.

2. Materials and Methods

A recent American Chemical Society review [2] on the use of catalysts in pyrolysis processing has "highly recommended" the two-stage pyrolysis-catalysis of waste plastics since advantages include;

- It facilitates decreasing the plastic viscosity, reducing thereby, both mass transfer and heat transfer problems in the subsequent catalytic cracking stage.
- The process is more controllable e.g. the temperature of each stage can be easily controlled.
- It is particularly suited to mixed plastic wastes, where any residues and dirt associated with the plastics remains in the pyrolysis unit.
- Using a two-stage reactor enables greater control of the catalytic process, less particulates are carried over which can de-activate the catalyst and the catalyst has a longer active life.
- Two-stage reaction systems improve the contact between pyrolysis products and the catalyst and enables the reacted catalysts to be recycled and reused.

The research will progress using two-stage pyrolysis-catalysis. Pyrolysis of the plastic waste occurs in the first reactor at ~ 500 °C. The evolved gases pass directly to the second catalyst stage, where depending on the type of catalyst and process conditions the targetted end-products can be obtained; (i) Using nickel-based silica or alumin catalysts at ~800 °C and in the presence of steam generates a hydrogen-rich syngas (ii) Using nickel based catalysts with added transition metal modifiers at ~800 °C produces carbon nanotubes (iii) Using Zeolite type catalysts at lower temperatures of ~ 500 °C can generate chemicals or (iv) gasoline. Figure 1 shows a typical two-stage pyrolysis-catalysis experimental system.

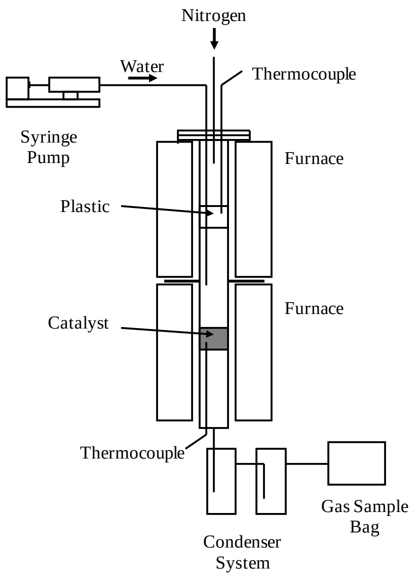

Figure 1. Schematic diagram of a two-stage pyrolysis-catalytic reactor

The Marie Skłodowska-Curie Action project plan involves;

→ bench scale collaboration on pyrolysis
→ development of catalysts for maximised production of the various high value products
→ incorporation of the catalysts into the combined two-stage pyrolysis-catalysis process
→ scale-up to pilot scale
→ product testing and comparison to standards & specifications
→ process modelling & simulation and techno-economic assessment.

3. Results and Discussion

There has been some research into the production of hydrogen from the thermal treatment of plastics with polyethylene, polypropylene and polystyrene among the feed-stocks investigated [4-12]. Research has centered on the use of nickel catalysts [3, 12]. Also, manipulation of the metal addition to the catalysts can significantly enhance the yield of hydrogen to more than 75 vol.% [12, 13]. The properties of the catalyst, pore size distribution, metal particle size (particularly nano-sized particles), support properties, etc have been shown to be important parameters [13]. Figure 2 shows the yield of hydrogen and other gases using a two-stage pyrolysis-catalytic reactor with an Ni-Mg-Alumina catalyst and in the presence of steam for the processing of polypropylene (PP), polystyrene (PS), high density polyethylene (HDPE), a real-world mixed plastic waste (waste plastic) and a synthetic mixture of the main plastics found in municipal solid waste and a mixed plastic waste (waste). High yields of hydrogen are found, derived from the steam reforming of the pyrolysis gases.

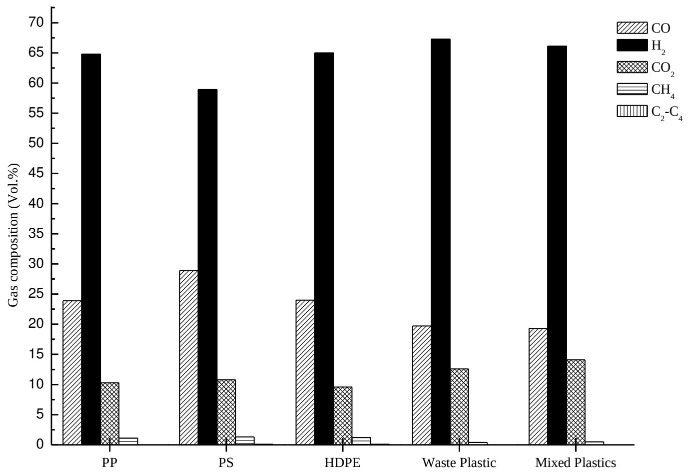

Figure 2 Gas compositions for the pyrolysis-gasification of plastics at gasification temperature of 850 °C

During pyrolysis-catalysis of waste plastics, there is commonly formation of carbon deposition on the surface of the nickel catalysts which can deactivate the catalyst. However, it has been shown [14-16], using transmission electron microscopy (TEM) and Raman spectroscopy analysis of the carbon deposits, that in some cases the carbon is composed of carbon nanotubes. Carbon nanotubes (CNT) have unusual and commercially important physical, mechanical and electronic properties. CNTs can be used for field transistors due to their low electron scattering. Lower quality CNTs can be used as fillers in metal and plastics composites which provides increased tensile strength [17]. Recent work has shown that CNTs and hydrogen can be produced simultaneously from plastic feedstocks. Figure 3 shows examples of carbon nanotubes produced from waste polypropylene using a two-stage pyrolysis-catalysis reactor with a Ni-Mn-Alumina catalyst in the presence of steam. The polypropylene was pyrolysed in the first stage via heating from ambient to 500 °C and the catalyst temperature was maintained at 800 °C. Interaction between Ni and the catalyst support plays a significant role in the process; weak metal support interaction for the Ni-Mn-Alumina catalyst (calcined at 300 °C) resulted in a lower hydrogen production and much higher yield of carbon products.

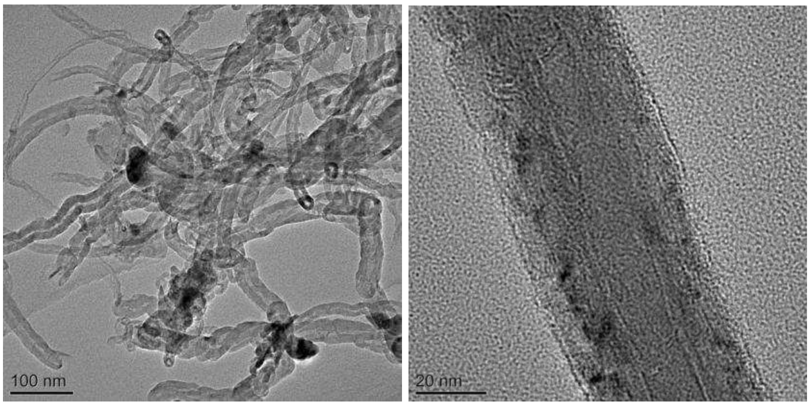

Figure 3. Transmission electron microscopy analysis of the reacted Ni-Mn-Alumina catalyst.

The composition of the product oils from pyrolysis of plastic waste are based on the original polymer structure. Kaminsky et al [19] reported that pyrolysis of polyethylene and polypropylene, produce an almost exclusively aliphatic oil consisting of alkanes and alkenes whereas polystyrene produces an oil high in concentration of the monomer, styrene and also other aromatic compounds. Pyrolysis of a mixed virgin plastic polyethylene and polystyrene produces oils with high concentrations of toluene, ethylbenzene and styrene [20]. Using catalysts in the pyrolysis process produces very high concentrations of individual chemicals. For example, Y-zeolite and ZSM-5 catalysts can dramatically increase the content of toluene, ethylbenzene and xylenes in the oil from pyrolysis-catalysis of polyethylene [21]. Keane [22] has suggested that the shape selectivity micropore-size properties and surface acidity of zeolite catalysts can be manipulated to produce narrow ranges of hydrocarbons. It has also been recently suggested that using mesoporous catalysts such as MCM-41 can also allow the manipulation of the product slate to produce targeted aromatic chemicals [2]. Figure 4 shows some araomatic chemicals found in the product oil from the two-stage pyrolysis-catalysis of various plastics using a ZSM-5 zeolite catalyst at 500 °C. The plastics were pyrolysed in the first stage and the pyrolysis gases were passed over the heated zeolite catalyst at 500 °C.

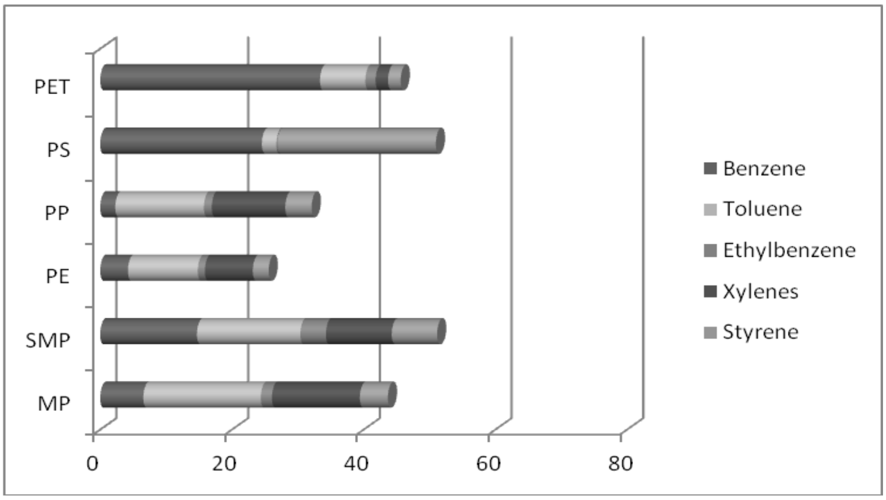

Figure 4. Yields of some selected aromatic compounds from the pyrolysis-catalysis processing of real world plastics (MP) the simulated mixture of plastics (SMP) and virgin plastics (PE, PP, PS, PET) with a zeolite ZSM-5 catalyst.

Several studies have employed catalysts added to the pyrolysis of waste plastics to improve the fuel quality of the oil product to give compositions similar to that of commercial fuel types [23, 24]. Most research has centered on the use of zeolite catalysts such as HZSM-5, MCM, NH_4Y, NaY since these are used in petroleum refineries for upgrading crude oil [23-25]. Figure 5 shows the yield high molecular weight hydrocarbons (C_{16+}) and fuel range hydrocarbons (C_5-C_{15}), from the pyrolysis-catalysis processing of real world plastics (MP) the simulated mixture of plastics (SMP) and virgin plastics (PE, PP, PS, PET) with a zeolite ZSM-5 catalyst. For the uncatalysed pyrolysis of the plastics, a high yield of oil/wax was obtained for the plastic material in the range of 81-97 wt.%. The yield of oil/wax decreased with addition of catalyst to between 44-51 wt.%, depending on the plastic with a resultant increase in gas yield. However, the composition of the pyrolysis-catalysis oils was significantly increased in aromatic hydrocarbon content.

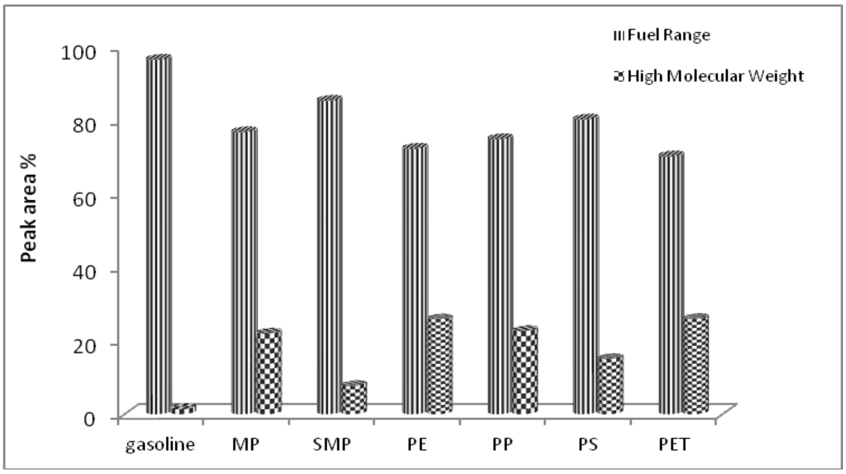

Figure 5. Influence of a zeolite ZSM-5 catalyst on the distribution of fuel range and high molecular weight compounds in pyrolysis-catalysis product oil from processing of real world plastics (MP) the simulated mixture of plastics (SMP) and virgin plastics (PE, PP, PS, PET) in comparison to gasoline.

4. Conclusions

The combined pyrolysis and catalysis of waste plastics offers the potential for a flexible processing technology. Careful use of the most suitable catalyst and control of the process conditions, enables the same reactor system to deliver high value products such as hydrogen, carbon nanotubes, chemicals and gasoline.

5. Acknowledgement

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowski-Curie grant agreement No. 643322 (FLEXI-PYROCAT). The support is gratefully acknowledged.

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