A two-stage pyrolysis/plasma reactor for the dry reforming of biomass pyrolysis products to increase syngas yield.

A. Carvell, M. Nahil and P.T. Williams

School of Chemical and Process Engineering, University of Leeds, Leeds, UK

Abstract: Gliding arc non-thermal plasma has been shown to be effective in dry reforming of methane, due to high flow rate capability and good selectivity. However very little is known about the effect of gliding arc on reforming the products of biomass pyrolysis. In this work we aim to address that gap in knowledge. Plasma alone is shown capable of converting CO_2 into CO and O_2 . Ni/Al₂O₃ is shown to increase syngas yield by 81% in a catalyst alone system, combination with gliding arc in a plasma-catalysis system will be investigated.

Keywords: Gliding arc, dry reforming, pyrolysis, syngas.

1. Introduction

Much of the global supply of basic chemical feedstocks is sourced from fossil fuels, finding renewable sources for these materials will be essential for a safe and sustainable future. The use of these fossil fuels results in huge quantities of greenhouse gas (GHG) emissions annually, particularly carbon dioxide (CO_2). Reducing these emissions is a key step in limiting the impact of global climate change.

Syngas, or synthesis gas, is a mixture of hydrogen and carbon monoxide that gets its name from its common use as an intermediate in Fischer-Tropsch synthesis, in which syngas plays a vital role in *synthesising* products such as methanol and ammonia, as well as many others. The majority of the global supply currently comes from steam reforming methane CH_4 [1].

Pyrolysis is a method of breaking down matter by thermal decomposition in an inert atmosphere. Pyrolyzing biomass produces a complex mixture of HCs, as well as H_2 , CO_2 and CO. Much of the available hydrogen and carbon is contained in the HCs. In order to maximize syngas yield these products can be reformed using one of three methods; steam reforming, dry reforming or partial oxidation [2].

Dry (CO₂) reforming of methane using catalysis, plasma and plasma-catalysis has been well researched as an alternative method for syngas generation [2,3]. Very little work has been done to investigate the dry reforming of $>C_2$ length hydrocarbons. Whilst issues such as carbon deposition on catalysts and scalability have limited the techniques adoption on industrial scale, the potential for carbon capture and utilization through dry reforming has kept research on the method progressing [2,4].

Non-thermal plasma (NTP) has been shown to be effective in converting CO_2 and methane, C_2 - C_4 and model tar compounds into syngas. However, the conversion rates are typically low and vary with the form of plasma used [3,5,6]. Compared with other NTP mechanisms gliding arc has more desirable characteristics for use in dry reforming pyrolysis products due to; the ability to operate at much higher flow rates, good selectivity and higher energy efficiency [6].

When used in combination with catalysts NTP has been shown to have synergistic effects on syngas production, capable of out performing plasma alone and catalyst alone systems, though this is dependent on conditions [6].

2. Experimental set up

In this work a novel two-stage pyrolysis-plasma reactor, shown in figures 1, will be used to investigate the effect of gliding arc NTP on the products of pyrolysis of real biomass. NTP has been investigated in the dry reforming of methane and some model compounds, however the effects on more complex mixtures of HCs are not yet well understood. This work will attempt to fill the gap in knowledge by testing plasma alone and plasma-catalysis set ups.



Fig. 1. Schematic of two-stage pyrolysis/plasma reactor.

The reactor, shown in figure 1, was designed with a closed 1st stage furnace where biomass samples held in a sample boat can be pyrolyzed. The carrier gas (N₂) delivers the gas to the 2^{nd} stage, a hinged furnace to allow for the insertion of the quartz plasma chamber. From the 2^{nd} stage the carrier gas and products pass through a condenser system, removing any liquid products, and into a gas sample bag for off-line analysis.

Initial work using a two-stage pyrolysis-catalyst reactor has been done to establish the most effective catalyst in the dry reforming reaction. From this work a Ni/Al₂O₃ catalyst outperformed the Co/Al₂O₃ and NiCo/Al₂O₃ catalysts tested in terms of syngas yield (38.7, 35.3 and 34.9 g/mol, respectively). As well as providing evidence for the most effective catalyst, this work will be used for energy efficiency comparison with the planned work on the pyrolysis-plasma reactor.

The experimental work on the two-stage pyrolysisplasma reactor will begin with a series of CO₂ conversion experiments to establish what trends may be seen by varying gas flow rate, CO₂ injection rate, plasma power and reactor temperature. Gas flow rate will be increased from a minimum of 2 L/min to a maximum of 5 L/min in 0.5 L increments. Total gas flow will not exceed 5 L/min as issues of pressure build up in the reactor begin to cause leaks above a certain flow rate. CO₂ injection rate will be done at 250 ml/min up to 2 L/min total injection. Above 2 L/min CO₂ injection will be done in 500 ml/min increments. Plasma power will be adjusted as power supplied from the mains to the reactor in 40 V increments between 120 V and 240 V. Reactor temperatures of 0-400 °C in increments of 100 °C will be investigated.



Figure 2. CO₂ conversion by gliding arc plasma in 50% and 60% CO₂ (50% and 40% N₂) in increasing voltage, total gas flow rate was 2.5 L/min, no heat was applied using the furnace.

Using the results from this first series of experiments 2 gas flow rates and 2-4 CO_2 injection ratios will be selected, depending on significance of the difference in conversion rate, for use in the following experiments.

Following the selection of 2-4 CO₂ injection rates model tar compounds, e.g. toluene, naphthalene, will be fed into the reactor to ascertain the effect of the gliding arc plasma on the dry reforming of these compounds. These compounds will also be fed through the reactor with no CO₂ to provide data on the effect of the gliding arc on the compounds themselves and to establish how the presence of CO₂ might alter those effects. The temperature will be kept above the boiling point of the model compound in use to prevent condensation in the reactor. In this stage of the work the effect of a catalyst in the 2nd stage will be investigated to establish its effect on the dry reforming of HCs. The catalyst used at this stage of the experiments will be Ni/Al₂O₃.

The bulk of the experimental work planned will be done by pyrolyzing real biomass in the 1st stage furnace and using the conditions established in the first series of experiments. As the focus of this work is the effect of gliding arc on the product of pyrolysis, the 1st stage conditions will be kept constant at 40 °C/min heating rate to 600 °C for a dwell time of 20 min. The experimental plan will follow the same as in the previous paragraph, with the addition of various catalysts. Optimal catalyst quantity and position relative to the plasma will be investigated first before progressing further. As the mixture of HCs produced will have a wide range of boiling points condensation cannot be completely avoided in this stage, temperature will be maintained at >200 °C.

3. Acknowledgements

I would like to thank the EPSRC for providing the funding to allow me to perform this investigation.

I would like to thank my supervisors, Prof Paul Williams and Dr Mohamad Nahil, for their guidance, patience and insights.

4. References

[1] Y. Gao, J. Jiang, Y. Meng, F. Yan, Energy Convers. Manag., **171**, 133 (1995).

[2] Z. Hou, P. Chen, H. Fang, X. Zheng, T. Yashima, Int. J. Hydrog. Energy, **31**, 555 (2006).

[3] X. Tu & J. C. Whitehead, J. Phys. D, 44, 9658 (2014).

[4] C. Liu, X. Y. Quek, W. Ni. E. Cheo, R. Lau, A.

Borgna, Y. Yang, Fuel Process. Technol., 58, 380 (2009).

[5] G. Petitpas, J-D. Rollier, A. Darmon, J. Gonzalez-Aguilar, R. Metkemeijer, L. Fulcheri, Int. J. Hydrog. Energy, **32**, 2848 (2007).

[6] W-C. Chung, M-B. Chang, Renew. Sust. Energ. Rev. **62**, 13 (2016).