Plasma reforming of waste derived syngas for downstream catalytic processes and biofuel applications

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Highlights

- Plasma reforming is applied to waste generated syngas for biofuel production
- More than 95% of tars are reformed, along with the majority of other hydrocarbons
- Reformed gas free of hydrocarbons is more suitable for catalytic transformation
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1. Introduction

Waste gasification has received increasing attention in the past two decades due to the growing demand for clean fuels and chemical feedstocks, as well as the need for reducing dependency on fossil fuels, lowering green house gas emissions and disposing of existing wastes [1]. The syngas produced by gasification contains high levels of condensable organics (or tars) and gaseous hydrocarbon species (acetylene, thiophenes, etc.) which can be problematic in subsequent catalytic stages for chemical synthesis. This is because metal based catalysts for chemicals and biofuels synthesis are extremely sensitive and can be easily poisoned or deactivated by these pollutants [2]. A particularly advantageous way to reform tars to simple gaseous products, thus contributing to the net calorific value (NCV) of the cleaned gas, is the use of secondary plasma refining. When used at high temperatures (thermal plasmas) the heat does also contribute to vitrify the ashes producing an inert and non-leachable product for use in pipe-bedding and construction, thus favoring the exploitation at large scales [3]. This work explores syngas plasma reforming at industrially relevant conditions for the purpose of process up-scaling and simplification, and investigates the potential for obtaining a gas product suitable for chemical transformation and high quality biofuels synthesis.

2. Methods

The experimental effort was directed at controlling the critical parameters and operating ranges of plasma-assisted tar reforming as they directly relate to the design of an industrial process. In order to avoid excessive boundary layer effects and provide realistic fluid, mechanical and thermal behavior of tars in commercial plant, experimental tests were performed in a moderately large scale demonstration plant (APP plant in Swindon, UK). Refuse Derived Fuel (RDF) from municipal solid waste was thermally treated in a steam-oxygen fluid bed gasifier at 700-800 ˚C to produce a raw quality syngas. The gas is then directed to the plasma arc, which is generated by a directly-transferred system (graphite electrode) positioned at the center of a cylindrical vessel. During operation, the power to the plasma arc is controlled in order to keep the slag in a molten state and maintain the temperature of gases exiting the unit to the desired temperature. Refined gas is then cooled to below 200 ˚C, and analyzed by continuous FTIR, and GC/MC analysis on filtered samples.

3. Results and discussion

Hydrocarbon gas conversions obtained after cracking tar vapors in a plasma converter reactor are shown in Fig. 1 for a residence time of ~2 s at different temperatures. The conversions are expressed on the basis of the raw/crude syngas fed to the converter and include hydrocarbons produced during the first stage of the gasification process. At 700 °C (gasifier exit temperature) very little cracking occurred, so apart from small increases in CH_4, concentrations of other species remain stable. As the plasma intensity is raised, hydrocarbon conversions increased rapidly, predominantly alkenes and to a lesser extent C_6H_6, and C_2H_2. At 800 °C the tars conversion rate passed through a maximum and eventually declined, with the result that at 1200 °C the major products are the pure syngas constituents, i.e. CO and H_2.

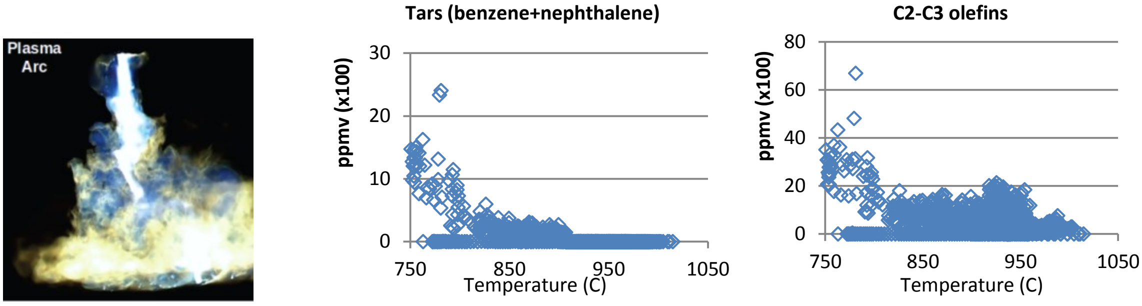

Figure 1. Plasma arc (left) and behavior of tars and C2-C3 olefins at different plasma intensities and thermal levels (right)

A key element of this work was to establish that the syngas from waste resources was of sufficient quality for catalyst operation. A single methanation stage (8%wt. Ni/Al_2O_3 catalyst) was operated on a continuous basis using refined syngas (<1% CH_4) as shown in Fig.2. This demonstrated, once stabilised, consistent catalyst activity over the period with CO conversion of 29% with consistent methane (~ 7% vol.) being produced. By way of a control, the same configuration was operated with the addition of untreated, raw syngas from the gasifier at 50% vol., upon condensation of tars and H_2S/HCl in conventional scrubbers, but with no plasma treatment. Methane yield initially increases due to presence of waste-derived alkanes at the inlet, but catalytic activity dropped significantly within 10h 15 minutes after testing had commenced. This demonstrated that, as expected, poisoning from trace contaminants (thiophenes) and carbon deposition causes swift deactivation of the catalyst, providing confidence that the gas quality achieved from waste derived syngas in this process is of sufficient quality for sustained synthetic natural gas (BioSNG) production in a multistage catalytic process.

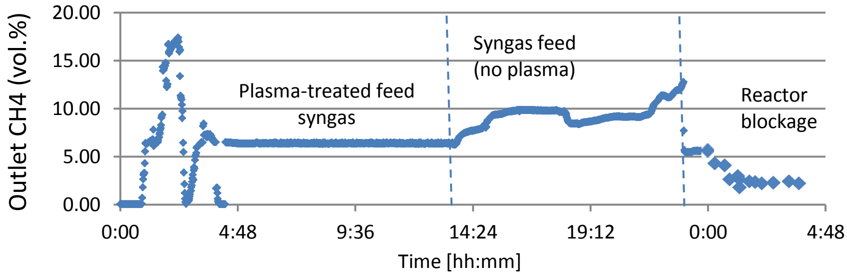

Figure 2. Methane production in methanation catalytic stage with and without plasma treated feed gas

4. Conclusions

H_2 and CO are observed to be the major products of plasma reforming, and formation of methane, and C2 hydrocarbons such as acetylene and ethylene, generally predicted by thermal kinetic models, was negligible. All these factors contribute to an almost complete conversion of tars to H_2 and CO, resulting in high syngas yield, low hydrocarbons products and nearly 100% carbon conversion efficiency at the plasma stage. This also ensures smoother and longer operation of subsequent catalytic processes for biofuel production.

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[3] M.Materazzi, P.Lettieri, L.Mazzei, R.Taylor, C.Chapman, Fate and behavior of inorganic constituents of RDF in a two stage fluid bed-plasma gasification plant, In Fuel,150, 2015, pp. 473-485

Keywords
Waste gasification; BioSNG; Plasma; Methanation.

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Education / Qualifications

2011-2015	**Ph.D. in Chemical Engineering,** UCL, UK. "Fundamental investigations on ashes and tar behaviour in a two stage fluid bed-plasma process for waste gasification."
2008-2011	**MSc**, **Chemical Engineering and En. Processes (with one year abroad)**, Universita degli studi dell'Aquila, Italy. Graduated with grade 110/110 *cum laude*.
2009-2010	**Diploma of International Study, Chemical Engineering,** University College London, UK.
2004-2008	**Laurea**, **Chemical Engineering,** Universita degli studi dell'Aquila, Italy. 110/110.
2015-2016	**Certificate in Learning and Teaching in Higher Education,** UCL, UK.

Professional History

Sep. '13 – Dec. '15	**Teaching Fellow (FHEA),** Dept. of Chemical Engineering, UCL
Jan. '16 – present	**Senior Research Fellow**, Department of Chemical Engineering, UCL, UK
Oct. '14 – Sep. '16	**Senior Process Engineer**, Advanced Plasma Power Ltd, UK
Sep. '16 – present	**Innovation and R&D Vice Director**, Advanced Plasma Power Ltd, UK

Selected Professional Bodies Committee member

- Elected member of the Engineering Physical Science Research Council (2016-present)
- IChemE PTSIG Committee Member (since 2014)
- Technical Director, Engineers Without Borders (EWB – UCL), (2012-2015)
- Safety Committee member of Engineering Faculty Sciences, UCL (2015-present)
- IWWG - International Waste Working Group (2017-present)

Consultancy

2016-present	GoGreenGas Ltd., Swindon, UK: BioH2 and *Biofuels synthesis from waste derived syngas*
2012-2013	NNL/Sellafield Ltd, UK: *Design and Operation of a 4/10th TDN fluid-bed reactor*
2014-2016	NNL/Sellafield Ltd, UK: *Nozzles design and lumps formation in TDN fluid-bed reactor*
2017-present	BioNano/British Council, UK: *Waste-to-Energy plant for waste treatment in Colombia.*

Awards and Other Achievements

2009 **Erasmus/Ferdinando Filauro Scholarships** for final year research project abroad (London, UK)
2012 **Departmental Rooke Award** in recognition of the academic achievements in first year of PhD.
2014 **Best Paper Award** 29th Int. Conference on Solid Waste Technology and Management, Philadelphia[20]
2016 **Nuclear Institute Prinketon Award** for the best paper of the year in the nuclear sector [15]
2015 **Royal Society of Chemistry (RSC)** Best Thesis Award (Energy Sector) in UK – Second Price
2015 **UCL Newton Memorial Prize** for research in Chemical Engineering, in recognition of "best academic achievements in the sustainability sector"

Research

My research and professional activity spans on several aspects of Waste-to-Energy technologies, with particular attention given to thermal treatments (combustion, gasification and pyrolysis) of different fuels and wastes, design and operation criteria of fluidized bed reactors for industrial application (including nuclear and renewable energy sectors), and reaction engineering and catalytic process design for Biofuel and BioSNG synthesis. My vision has been to push the boundaries of research into fluidization processes for sustainable development, working innovatively and collaboratively, across disciplinary interfaces.

Applications of my research cover chemical, petrochemical, nuclear and energy-from-waste industries. My research has been supported by sustained funding from Industry, British Council, Energy Technology Institute (ETI), Department for Transport (DfT), with funding as PI and Co-I totalling over **£1.5M**. I have graduated 12 MSc and Meng students, recipients of a number of awards 2 of which are in academic posts and the others in industry. My research in fluidization has advanced the state-of-the-art through innovative experimental and modelling techniques linking fluidization with plasma technologies and advanced computational fluid-dynamic modelling, specializing on the investigation of the effect of process conditions on fludization through X-ray imaging. My work in fluidization has received international recognition, including 2 invited plenary & keynote lectures at major international conferences [24-26]. My publications include 3 book chapters and over 15 refereed articles. In October 2016 I published my first book 'Clean energy from waste'[1] which has been downloaded a record 1600 times since publication (Sept'17 Springer Bookmetrix record). I am currently writing a book on BioSNG from Waste for Elsevier.

Knowledge Transfer - I have an established track record of strong and continued collaboration with industry through consultancy, research contracts and studentships, including Shell, Advanced Plasma Power (APP), Progressive Energy Ltd, Catal Ltd, GoGreenGas, Air Products, National Nuclear Laboratory, Nuclear Decommissioning Authority and Sellafield Ltd. The direct impact of my research in fluidization and plasma catalysis contributed to the development of the Gasplasma process at APP. My work with APP was key for the development and scale-up of their Gasplasma demonstration plant into the first semi-commercial (20MWe) scale fluid-bed/plasma waste gasification plant in the UK. Before that, I designed part of the pilot plant (60 kWth) for BioSNG production from syngas. This has allowed rapid assessments of different scales, configurations and feedstock types for biofuel production at larger scale. Tests on smaller scale reactors, lead and directed by myself, have also contributed widening the commercial opportunities of the company in the fuel synthesis sector. My work as a consultant with NNL and Sellafield Ltd. has contributed to solve operational problems and increase throughput of the Magnox TDN fluid-bed reactors for spent fuel finishing operated at Sellafield. The study resulted in a series of modifications which have been implemented on plant and enabled achieving optimal and safe operation of the TDN to complete its delivery programme by 2020.

Main Publications:

Books and Book Chapters

1) Materazzi, M. (2016). "Clean energy from waste: fundamental investigations on ashes and tar behaviour in a two stage fluid bed-plasma process for waste gasification". Springer ThesEs Publishers. ISSN 2190-5053

2) Materazzi, M. (2016). Conversion of biomass and waste fuels in fluidised bed reactors. In Springer (Ed.), Yates, J., Lettieri, P., *Fluidised bed reactors: Processes and Operating Conditions* (pp. 111-135).

3) Materazzi, M., & Lettieri, P. (2017). Fluidised beds operation in waste thermal treatment. In M. Morbidelli, & R. S. O. C. G. Britain (Eds.), *Chemistry, Molecular Sciences and Chemical Engineering. Electronic Encyclopaedia*. Elsevier Publishing.

4) Materazzi, M., & Lettieri, P. (2017) Advanced X-ray imaging for fluidised bed operations. In M. Morbidelli, Britain (Eds.), *Chemistry, Molecular Sciences and Chemical Engineering, Electronic Encyclopaedia*. Elsevier Publishing.

Journal Publications

5) Materazzi, M., Lettieri, P., Mazzei, L., Taylor, R. Chapman, C. (2014) Tar evolution in a two stage fluid bed-plasma gasification process for waste valorization. *Fuel Processing Technology*, 128, 146-157.

6) Materazzi, M., Lettieri, P., Mazzei, L., Taylor, R., & Chapman, C. (2013). Thermodynamic modelling and evaluation of a two-stage thermal process for waste gasification. *Fuel*, 108, 356-369.

7) Materazzi, M., Lettieri, P., Taylor, R., & Chapman, C. (2016) Performance analysis of RDF gasification in a two stage fluidized bed–plasma process. Waste Management 47, 256-266.

8) Materazzi, M., Lettieri, P., Mazzei, L., Taylor, R., & Chapman, C. (2015) Fate and behavior of inorganic constituents of RDF in a two stage fluid bed-plasma gasification plant. Fuel 150, 473-485.

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10) Materazzi, M., Lettieri, P., Taylor, R., & Chapman, C. (2015) The Fate of Ashes and Inorganics in a Two-stage Fluid Particle System for Waste Valorization. Procedia Engineering 102, 936-944

11) Materazzi, F Grimaldi, PU Foscolo, P Cozens, R Taylor, C Chapman. (2017) Analysis of syngas methanation for bio-SNG production from wastes: kinetic model development and pilot scale validation Fuel Processing Technology 167, 292-305

12) Materazzi, P Lettieri, JM Dodds, A Milliken. (2017) X-ray imaging for design of gas nozzles in large scale fluidised bed reactors. Powder Technology

13) Panariello, M Materazzi*, R Solimene, P Salatino, P Lettieri. (2017) X-ray imaging of horizontal jets in gas fluidised bed nozzles. Chemical Engineering Science 164, 53-62. * *Lead Author*

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15) Materazzi M., Holmes, R., Gallagher B.. 3D printing and X-ray imaging applied to thermal denitration at Sellafield, Nuclear Future (Journal of the Nuclear Institute) Vol. 11 Issue 6 Nov/Dec 2015 ISSN 1745 2058.

16) Materazzi, M., P Cozens, R Taylor, C Chapman. Performance Analysis of syngas methanation for bio-SNG production from wastes in a pilot plant. Fuel Processing Technology *(Submitted, Under revision)*

17) Materazzi, M., P Lettieri, JM Dodds, A Milliken. Study of lumps segregation in a scaled-down TDN fluidised bed reactor. Powder Technology *(Submitted, Under revision)*

18) Panariello, L., M Materazzi, R Solimene, P Salatino, P Lettieri. Experimental and numerical analysis of jet penetration and gas evolution in a single-nozzle distributor fluidised bed. Chemical Engineering Science *(Submitted, Under revision)*

Selected Talks and Plenary Lectures

19) Materazzi, M., Lettieri, P., Taylor, R., Chapman, C. (2014) The fate of ashes and inorganics in a two-stage fluid particle system for waste valorization in 7th World Congress on Particle Technology (WCPT7), Beijing, 19-22 May, China.

20) Materazzi, M., Lettieri, P., Taylor, R., Chapman, C. (2014) Reforming of Light Volatiles and Aromatic Compounds in Advanced Thermal Treatments of Municipal Solid Wastes, in 29th International Conference on Solid Waste Technology and Management, Philadelphia, PA, March 30-April 2, USA.

21) Materazzi, M., Lettieri, P., Taylor, R., Chapman, C. (2013) Technical Aspects and Thermodynamic Evaluation of a Two Stage Fluid Bed-Plasma Process for Solid Waste Gasification in "Sardinia 2013 - 14th International Waste Management and Landfill Symposium (Sardinia 2013), IWWG, S. Margherita di Pula 30 Sept – 4 Oct., Italy.

22) Materazzi M., Lettieri P., Mazzei L., Taylor R., Chapman C., (2013) Thermodynamic evaluation of a two stage fluid bed-plasma process for solid waste gasification. Proc. Fluidization XIV, May 25-30, 2013, Leeuwenhorst Noordwijkerhout, The Netherlands.

23) Materazzi, M., P Lettieri, JM Dodds, A Milliken X-Ray Imaging for Design of Gas Nozzles In Large Scale Fluidised Bed Reactors, Fluidization XV - A ECI Conference Series May 22-27, 2016, Fairmont Le Chateau Montebello, Quebec, Canada.

24) Materazzi, M., P Lettieri, JM Dodds, A Milliken. Magnox Reprocessing Thermal Denitration [TDN] Reactors: Utilising 3D Printing and X-Ray Imaging to ReDesign and Test Fluidising Air Nozzles – WM2016 Conference March 6 - 10, 2016 Phoenix AZ.

25) Materazzi M. Climate Change and Sustainability: New Challenges for the UK Innovation Policy in the Waste Management Sector. Focus on Biofuels, 7th International Symposium on Energy, Manchester England, 13-17 August 2017

26) Materazzi M. New Frontiers of Plasma reforming in Advanced Thermal Treatments for biofuel production from wastes. 16th Waste Management and Landfill Symposium, (Sardinia 2017), IWWG, S. Margherita di Pula 2 – 6 Oct., Italy