Institution: University of Nottingham		
Unit of Assessment: 12		
Title of case study: New pyrolysis techniques delivering improved fuel additives and contributing to UK energy policy development		
Period when the underpinning research was undertaken: 2000-2019		
Details of staff conducting the underpinning research from the submitting unit:		
Name(s):	**Role(s) (e.g. job title):**	**Period(s) employed by submitting HEI:**
Colin Snape Will Meredith	Professor Assistant Professor	07/2000 to present 06/2001 to present
Period when the claimed impact occurred: 08/2013 to 07/2020		
Is this case study continued from a case study submitted in 2014? N		

1. Summary of the impact

Government policy and product innovation (with regards to fossil fuels) rely in part on the ability to characterise organic macromolecules. New, non-destructive, high-pressure pyrolysis techniques, developed in the Faculty of Engineering, are now able to do this. The techniques were utilised by Global chemical company, Innospec, to overcome engine failures caused by deposits found in fuel injectors. Since 2013, the findings have informed the development of 10 new fuel additives (total sales revenue USD200,000,000); influenced the strategic direction of their fuel additive business (annual sales revenue of approximately USD600,000,000) and played a key role in protecting the company's reputation. The techniques also produced a robust estimate of the UK's shale gas reserves which was published in Nature Communications. This sparked a public debate about the UK's shale gas policy during a public engagement campaign, which generated significant press interest (referenced by 384 media articles across 10 countries). In 2019, the Scottish Government directly cited the published research in a speech to the Scottish Parliament, where they announced their final policy position not to support unconventional oil and gas development (i.e. fracking) in Scotland.

2. Underpinning research

Over the last 20 years, Prof Snape and Dr Meredith have developed and implemented two specific high-pressure pyrolysis techniques: hydropyrolysis and high-pressure water pyrolysis.

<u>Hydropyrolysis (HyPy): A high hydrogen pressure technique for the characterisation of organic macromolecules and combustion residues</u>

Analytical pyrolysis is an established technique for the molecular characterisation of organic macromolecules. However, pyrolysis tends to use fast heating rates, approximately 1000ºC/s, and a temperature of up to 750ºC, which results in the breakdown of the released products, low overall yields and poor reproducibility. Long term support totalling GBP631,372 from NERC [7-10] between 2001 and 2012, enabled Prof Snape and Dr Meredith to address these challenges by developing the hydropyrolysis technique (HyPy) [1]. The research developed a novel procedure combining slow heating (8ºC/min to 550ºC), high hydrogen pressure (150 bar), a molybdenum catalyst and product collection on dry-ice cooled silica. This arrangement allows direct thermal desorption gas chromatography - mass spectrometry (GC–MS), which identifies the different components in the product. As such, HyPy has the unique ability to create a highly selective molecular "fingerprint" that was not possible with traditional analytical pyrolysis techniques [1]. This enhanced compositional selectivity has allowed HyPy to provide valuable insights into the formation, evolution and fate of organic matter in rocks, oils, sediments and soils [2].

The technology was licensed and successfully commercialised in 2008, in partnership with UK SME Strata Technology Ltd. It overcame the challenges of ensuring safe operation, whilst employing high pressures of explosive hydrogen gas at elevated temperatures. The HyPy technology was fundamental to subsequent collaborative research [3,4] from 2010 with Innospec Ltd, a multi-national speciality chemical company and the world's largest dedicated fuel additive supplier.

Innospec's fuel additives increase the efficiency and extend the life of engines. They do this by mitigating the formation, and allowing the removal, of deposits in the engine which can cause blockages to the fuel injector. Modern engines run at higher temperatures and pressures to meet emissions targets. As a result, injectors are more susceptible to blockage from combustion residues formed within the engine as well as other deposit sources. These residues are solvent insoluble and difficult to analyse by traditional chromatographic or spectroscopic techniques. Innospec funded University of Nottingham (UoN) research [3,4] to characterise these deposits, and so assist in the development of deposit control additives (DCAs). HyPy has the unique ability to hold entire injector needles within the reactor, and so can thermally break down and then characterise the deposits at a molecular level by GC-MS [3]. In 2014, HyPy was used in conjunction with other molecular imaging techniques, allowing the UoN team to understand how "non-commercial" low molecular weight polyisobutylenesuccinimide (PIBSI), might form deposits [4]. This work proved that Innospec additives were fully soluble within the fuel, and not a source of damaging deposits. It also proved that the source of such deposits was non-commercial low molecular weight PIBSI.

High-pressure water pyrolysis to simulate natural oil and gas generation

From 2004, the UoN team continued to develop the knowledge and expertise arising from HyPy [1] in order to investigate the role of water pressure on hydrocarbon generation, maturation and cracking [3]. By 2009, the UoN team had developed the unique capability to use high-pressure liquid water during the artificial maturation of petroleum source rocks [5].

Traditionally, water vapour pressure has been used to artificially mature rock to generate oil and gas in a technique known as hydrous pyrolysis. However, in the subsurface of the earth, due to lithostatic pressures (the stress exerted on a body of rock by the surrounding rock) water is only present in its liquid phase. The UoN high pressure liquid water capability 'using liquid water as the pressuring medium' has shown that high pressures of up to 1000 bar can significantly hamper source rock maturation, petroleum generation and also oil-to-gas cracking [5]. This contrasts with the view previously held by the geoscience community that only pressure and temperature are important. As the lithostatic pressure increases with depth below the Earth's surface, this means that oils should be more stable at greater depths than previously thought in natural systems. With further recent funding from NERC of GBP254,307 [11], in 2019 the methodology was used by UoN researchers to show that high thermal maturities are required to generate dry gas (i.e. rich in methane), as typically found in shale gas systems. This suggested that estimates of total shale gas resources in the UK were a factor of 5 to 10 too high [6].These findings were later published in Nature Communications.

3. References to the research (Authors affiliated to UoN highlighted in **bold**)

[1] **Meredith, W.**, **Russell, C. A.**, **Cooper, M.**, **Snape, C. E.**, Love, G. D., Fabbri, D., & Vane, C. H. (2004). Trapping hydropyrolysates on silica and their subsequent thermal desorption to facilitate rapid fingerprinting by GC–MS. *Organic Geochemistry*, 35(1), 73-89. https://doi.org/10.1016/j.orggeochem.2003.07.002

[2] Hoshino, Y., Poshibaeva, A., **Meredith, W.**, **Snape, C.**, Poshibaev, V., Versteegh, G. J., ... & Naeher, S. (2017). Cryogenian evolution of stigmasteroid biosynthesis. *Science Advances,* 3(9), e1700887. https://doi.org/10.1126/sciadv.1700887

[3] Barker, J., Reid, J., **Snape, C.**, & **Scurr, D.** (2012). A novel technique for investigating the characteristics and history of deposits formed within high pressure fuel injection equipment. *SAE International Journal of Fuels and Lubricants*, 5(3), 1155-1164. https://doi.org/10.4271/2012-01-1685.

[4] Barker, J., Reid, J., **Snape, C.**, **Scurr, D.**, & **Meredith, W.** (2014). Spectroscopic studies of internal injector deposits (IDID) resulting from the use of non-commercial low molecular

weight polyisobutylenesuccinimide (PIBSI). *SAE International Journal of Fuels and Lubricants*, 7(3), 762-770. https://doi.org/10.4271/2014-01-2720

[5] **Uguna, C. N.**, Carr, A. D., **Snape, C. E.**, & **Meredith, W.**, **Diaz, M. C.** (2012). A laboratory pyrolysis study to investigate the effect of water pressure on hydrocarbon generation and maturation of coals in geological basins. *Organic Geochemistry*, 52, 103-113. https://doi.org/10.1016/j.orggeochem.2012.09.003.

[6] **Whitelaw, P.**, **Uguna, C. N.**, **Stevens, L. A.**, **Meredith, W.**, **Snape, C. E.**, Vane, C. H., ... & Carr, A. D. (2019). Shale gas reserve evaluation by laboratory pyrolysis and gas holding capacity consistent with field data. *Nature Communications*, *10*(1), 1-10. https://doi.org/10.1038/s41467-019-11653-4

Grants

[7] UoN PI: Prof Colin Snape; **Establishing the potential of hydropyrolysis to provide reliable molecular fingerprints for biodegraded crude oils and contaminated sediment cores;**. 2001–2002; NERC (NER/T/S/2000/01366); GBP33,202 https://ukerc.rl.ac.uk/cgi-bin/ercri5.pl?GChoose=gregcat&GRN=NER/T/S/2000/01366&GrantRegion=5&GrantOrg=69

[8] UoN PI: Prof Colin Snape; **Developing hydropyrolysis to generate molecular biomarker signals for solving key problems in oil exploration where conventional biomarker approaches fail;** 2002–2004; NERC (NER/T/S/2001/01153); GBP84,029 http://gotw.nerc.ac.uk/list_full.asp?pcode=NER%2FT%2FS%2F2001%2F01153

[9] UoN PI: Prof Colin Snape; **Developing hydropyrolysis and allied innovative high-pressure techniques for applications in oil exploration and detection of steroid abuse;** 2004-2006; NERC (NE/C507002/1); GBP51,068 http://gotw.nerc.ac.uk/list_full.asp?pcode=NE%2FC507002%2F1

[10] UoN PI: Prof Colin Snape; **Establishing hydropyrolysis as an effective technique for the determination and isolation of pyrogenic carbon in samples from the natural environment;** 2009–2012; NERC (NE/F017456/1); GBP463,073 https://gtr.ukri.org/projects?ref=NE%2FF017456%2F1

[11] UoN PI: Prof Colin Snape; **An integrated assessment of UK Shale resource distribution;** 2018–2022; NERC (NE/R018030/1); GBP254,307 https://gtr.ukri.org/projects?ref=NE%2FR018030%2F1

4. Details of the impact

The research described in section two has resulted in 2 areas of significant impact:

(1) Contributing to the development of new products and influencing the strategic direction of Innospec's USD600,000,000 fuel additive business

Innospec is a multi-national speciality chemical company (annual revenue in 2019/2020 of USD1,500,000,000) and is the largest dedicated fuel additive supplier in the world, with sales worth USD600,000,000 (2019/20). Since 2006, Innospec have funded GPB260,000 of research at UoN, which has resulted in numerous impacts for Innospec. These are described below (all quotes provided by their Senior Vice President and Chief Technology Officer in evidence letter [a]).

Solid deposits found in diesel engine fuel injectors (or their nozzles) cause significant issues for the 412,000,000 injectors produced each year. These deposits can have a number of negative effects on engine performance, including power loss, rough engine running and increased emissions. These effects have led to well documented vehicle failures. Innospec collaborated with the UoN to use HyPy [1,2,3,4] to develop a mechanistic understanding of the composition and morphology of fuel injector deposits. In 2012, for the first time, the UoN team demonstrated that injector deposits consist of layers of different chemical composition. The key finding from this work was that one additive chemistry would not be sufficient to reduce, or eliminate, all of the deposits. This new understanding influenced the strategic direction for Innospec's fuel additives business (annual revenue USD600,000,000), and the decision to develop and expand their fuel package offerings [a].

The UoN research findings have provided Innospec with the necessary knowledge to develop effective deposit control additives (DCA) thereby providing a solution to a key industry problem of internal diesel injector deposits (IDID).

As stated by Innospec regarding the research activities since 2013, "*The development of a much more detailed mechanistic understanding of fuel injector and filter deposits (composition and morphology), supported by numerous analytical results [HyPy], has been invaluable in keeping us at the forefront of fuel additive development…… Using the understanding obtained from the collaborative research with Nottingham, we have been able to develop bespoke fuel additive technology, resulting in the successful commercialisation of 10 new additives with a combined sales revenue of over $200million" [a]*

The researchers were also able to demonstrate [4] that existing fuel additives, manufactured by Innospec, did not cause harmful deposits in diesel engines. This ensured Innospec's reputation was maintained and prevented loss in sales of their fuel additive products. A statement from Innospec [a] declared, *"One of the projects with Professor Snape resulted in a crucial role in protecting Innospec's reputation, by proving that harmful deposits found in diesel engines and injectors were not related to the fuel additives manufactured by us."*

The development of these effective fuel additives has wider impacts, as described by the Senior Vice President, Innospec, "*The successful commercialisation of new fuel additive packages has given the major UK fuel suppliers the confidence to supply fuels, which prevent vehicle failure and poor engine performance. Whilst it is difficult to quantify the impact of these fuel problems, the number of injector failures worldwide is known to be high, with a single injector replacement costing ~$1000. Moreover, the reduction in greenhouse gas emissions, due to improved fuel economy benefits, should not be ignored."* [a].

(2) Informing UK energy policy and public debate regarding the potential of UK shale gas reserves

The UoN paper [6], which described the use of high-pressure water pyrolysis to assess the shale gas resource of the major UK shale formation (Bowland), was published in Nature Communications in August 2019. This research provided a more robust assessment of reserves, supporting the conclusion that the UK Government model, predicting approximately 50 years of economically recoverable shale gas, is incorrect by an order of magnitude. This revised assessment equates to less than 10 years of economically recoverable reserves based on current UK gas consumption.

The research was the sole publication referenced by the Scottish Minister for Energy Connectivity and the Islands, in a speech to parliament (3rd October 2019) announcing the Scottish Government's final policy position to not support unconventional oil and gas development (i.e. fracking). In this debate the minister stressed the importance of evidence in forming their decision, and directly quoted the UoN research when urging the UK government to change their position on fracking [b].

The research generated significant press interest and was referenced 384 times (337 articles and 47 broadcast) in the media across 10 countries. This included featuring in the BBC News at Ten and articles by the BBC (web reach: 17,294,123), The Guardian (web reach 84,859,005), The Telegraph (web reach 36,470,936) and The Daily Mail (web reach 55,365,115) [c].

5. Sources to corroborate the impact

[a] Corroborating letter from Innospec Inc.

[b] Scottish Parliament debate transcript 03/10/2019; https://www.parliament.scot/parliamentarybusiness/report.aspx?r=12293

[c] Media/press coverage statistics and reach of shale gas research in Nature Communications