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Environmental Chemistry Group **www.rsc.org/ecg**

Bulletin

The conversion of waste into chemical products and energy, for example by pyrolysis and gasification, was the theme for this year's **Distinguished Guest Lecture & Symposium** held on March 14th 2012 at Burlington House, London. The guest lecture, entitled "Fuels, chemicals and materials from waste," was given by **Professor Paul T. Williams**, University of Leeds. Other speakers covered the UK government position on energy from waste, the production of high-value chemicals, the planning and environmental impacts of pyrolysis and gasification, and the anaerobic treatment of municipal organic waste in composting facilities. A meeting report and articles based on presentations at this meeting may be found on pages 3-12 of this issue.

Reports from a meeting on

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Contents

Raffaella Villa (Cranfield University) spoke on “Organic waste disposal: emissions and risks.” Her quote from Richard Buckminster Fuller is a wonderful expression of the lack of legal, political, financial and scientific imagination when it comes to the management of waste:

3Pollution is nothing but the resources we are not KDUYHVWLQJ :H DOORZ WKHP WR GLVSHUVH EHFDXVH ZH¶YH EHHQ LJQRUDQW RI WKHLU YDOXH ´

Raffaella described her studies of the anaerobic treatment of municipal organic waste in composting facilities. Heat can be obtained from biogas production (methane and carbon dioxide), but odour problems are ubiquitous and like all odour issues, they are famous for their difficulties. Studies of bioaerosol emissions have shown that for the most part they declined quickly from the source, although anomalous and unexplained maxima in atmospheric bioaerosol concentrations were observed some distance away from the plant. As with all EfW processes, feedstock content and consistency are problematic; there are seventy different types of waste which can be used in an anaerobic digester, and seventy

been used on tyre pyrolysis oils and plastics pyrolysis oils with a view to produce a highly aromatic oil, which can be used as a chemical feedstock. For example, use of a two-stage pyrolysis-zeolite catalysis reactor transforms the tyre pyrolysis oil to a highly aromatic oil containing ~50 wt% of benzene, xylene and toluene.

The recovery of high-value materials from wastes using pyrolysis technology has, for example, included the recovery of carbon fibres from plastic composites. Carbon fibres are highly valuable materials that are used extensively in the aerospace and automotive sectors. Pyrolysis thermally decomposes the composite plastic to oil and gas, leaving the residual carbon fibre and some char. The char is amorphous and easily separated from the carbon fibre by mild oxidation, producing a recovered carbon fibre with strength properties takes place. The condensed product is then further distilled to produce a heavy oil, a medium oil and a light oil, with the off-gases combusted to raise steam.

Other commercial plants use fast pyrolysis of biomass wastes such as forestry or agricultural wastes to produce bio-oil. For example, Ensyn (Canada) have developed an entrained flow, rapid heating fast pyrolysis system to produce an oil product for use as a chemical feedstock and fuel oil. The biomass interacts with hot sand at ~500 °C and is very rapidly heated to produce fast pyrolysis primary products, which are then rapidly quenched to produce a liquid bio-oil product. Dynamotive (Canada) uses biomass wastes such as sawdust or bagasse (the fibrous matter that remains after sugarcane processing). These wastes are fed into a fluidised bed reactor, where fast pyrolysis at 500 °C occurs. Conversion of the biomass produces bio-oil (60 to 75 wt%), char (15 to 20 wt%) and non-condensable gases (10 to 20 wt%).

Gasification

Gasification converts hydrocarbon materials into a syngas at high temperature in the presence of oxygen in the form of air, steam, CO_2 or pure oxygen. It has been extensively used for coal gasification, but has also been extended as an energy technology for processing biomass, sewage sludge, municipal solid waste etc.

Gasification in the presence of air reduces the calorific value of the produced gases. For example, air gasification of biomass normally produces a gas with a calorific value between 4 and 7 MJ/Nm^3, whereas gasification with oxygen/steam generates gases with higher calorific values (10 to 18 MJ/Nm^3). However, air gasification has the advantages of low energy input and low tar content in the gaseous stream. Oxygen gasification is not common due to the high cost of producing oxygen. Steam gasification is attracting increasing interest because it produces gases with a high H_2 content.

The tar produced from gasification results in downstream problems, including tar blockages, plugging and corrosion in downstream fuel lines, filters, engine nozzles and turbines. Specifications of the tar content in the product syngas is normally less than 100 mg/Nm^3 for internal combustion engines, and 5 mg/Nm^3 for gas turbines, whereas the tar content in the product gas is generally 10 g/Nm^3 for air-blown fluidised bed gasifiers and 0.5 to 100 g/Nm^3 for the other types of gasifiers. Tar reduction methods include in-process catalytic cracking of the tar or downstream processes such as high temperature cracking of the tar to gas, hot gas filtration, or wet gas cleaning with equipment including spray towers, scrubbers etc.

A range of technologies have been developed to gasify wastes. The fixed bed reaction system is one of the most common processes used for gasification. Two basic types of traditional fixed-bed gasifiers are up-draft (counter-current) and down-draft gasifiers (co-current). Both these fixed-bed reactor types are based on natural slowly descending fuel flow caused by gravity. In an updraft gasifer, the feed is fed to the top of the gasifier and flows down slowly through drying, pyrolysis, reduction and oxidation zones. In a downdraft gasifier, the feed and the gasification agent (air) move in the same direction. The volatiles from pyrolysis pass through the oxidation zone, where the tar is partly crackis

19,000 to 165,000 tonnes per annum. For example, the Ebara TwinRec gasifier (Figure 3) in Kawaguchi, Japan processes 125,000 tonnes per annum of municipal solid waste and has been operational since 2002. The technology is based on a fluidised-bed gasifier, which produces a syngas that is combusted at high temperature (1350 to 1450 °C) in a cyclonic combustion chamber to raise steam for electricity production or district heating.

Combined pyrolysis-gasification plants also exist, notably the Thermoselect system with 6 plants operating in Japan

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Since the 2003 Waste Emissions Trading Act came into force, the UK government, in collaboration with the waste industry, has actively worked towards the diversion of organic waste from landfill and towards a “zero” landfill economy. Different types of waste classed as “organic” include agricultural waste, such as slurries and manure (~90 million tonnes/year), food and green waste (~20 million tonnes/year) and sewage sludge (~1.5 million tonnes/year).[1] The assessment and quantification of this organic fraction within mixed waste is pivotal for diversion targets and energy recovery.

Renewable energy from waste

Renewable energy from waste has an important role to play in tackling climate change by displacing the use of fossil fuels and by providing a more environmentally sustainable method of disposing of residual wastes, where recycling is not practical or economically feasible. Energy can be recovered from waste using a number of processes, including anaerobic digestion (AD), combustion, gasification and pyrolysis; each is capable of delivering sustainable methods of waste treatment and a clean source of energy. The recovery of energy from biomass-derived waste materials is supported by the Renewables Obligations (RO) as a mechanism to incentivise investment in suitable renewable energy production technologies. Where a heterogeneous fuel, such as mixed wastes, is used there is a requirement to understand what proportion of the total energy recovered is from a renewable resource, such as biomass. Work has been undertaken at Cranfield University, funded by TSB/SBRI with Defra and DECC, to develop appropriate methods of assessing the biogenic biomass content of mixed wastes, and the energy outputs from this fraction. This work involved the further development of an image analysis method previously devised at Cranfield University.[2]

The methods we developed demonstrate the capability to determine the biogenic proportion of mixed waste materials, and also to reliably estimate the net calorific value (NCV) of this fraction, which is indicative of the energy yield before process efficiency is taken into account. The net energy potential is calculated from measurements of the moisture content, which enhances the accuracy of the method. The moisture content is determined using a novel microwave technique developed by the National Physical Laboratory

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chain from waste input to end use of the AD residue. In practice, critical control points at each stage of the process chain provide opportunities to actively reduce risk. Under normal operating conditions, with the application of good practice, barriers (management measures) can be applied that will effectively guard against exposure to hazards.

Rational and, where possible, evidenced judgements about the likelihood and significance of receptor exposure to physical, chemical and biological hazards are coded. Most concern should be given to situations where significant hazards are readily available to receptors (e.g. direct ingestion), i.e. where potent, hazardous constituents in input streams remain unaffected by AD treatment and can migrate through the environment in sufficient quantities to cause harm. Hazard profiles containing a high concentration of animal and human pathogens appear near the top of the table, together with wastes derived from the leather industry containing high concentrations of chemicals. Pathways of high availability have no significant exposure barriers to certain hazards (direct ingestion). The end-uses that received the highest exposure ranking were ready to eat crops and grazing and animal feed as they offer the highest number of available pathways. The matrices highlighted that greater opportunities for exposure to hazardous agents occur with higher contaminated wastes for certain end-uses. These conclusions offer insights into where controls might be most effective; through (1) the exclusion of certain waste types; (2) the application of codes of practice backed up by the quality protocol for specific exposure routes and (3) specific attention being given to certain end uses. The approach explicitly linked expert understanding on waste categories, AD processes and the environmental fate of contaminants in the context of AD product end use and has highlighted the key drivers of potential exposure, providing a basis for control through the ADQP.

Bioaerosols and composting

The composting process relies on the proliferation of micro-organisms to decompose solid organic waste feedstock in order to produce a stable, organic material (compost). However, this process releases these micro-organisms into our understanding of the dose or amount of bioaerosols that people are exposed to, as a first step to closing this knowledge gap.

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Introduction

The world faces fundamental environmental issues and challenges. Human activities have led to substantial and potentially irreversible loss in the diversity of life, brought about through changes to ecosystems to meet rapidly growing demands for natural resources such as food, fresh water, energy and materials.[1] Monitoring the state of the natural environment is essential to identifying environmental problems, helping to understand drivers of change and testing the effectiveness of national and international policies to reverse declines. In addition, governments have a multitude of legislative and statutory obligations and commitments to meet. Measuring and monitoring the natural environment provides evidence for such reporting obligations[2] and underpins the development of environmental policies.

The ongoing economic crisis has left many governments with large budget deficits. One solution is the reduction of government expenditure. For ex[illegible] poli

Nature Conservation Committee (both BTO and the BRC) and the Natural Environmental Research Council (supporting the BRC).

Monitoring atmospheric pollutants

The National Ammonia Monitoring Network (NAMN)[18] is part of the UK Eutrophying and Acidifying atmospheric Pollutants (UKEAP) network which has measured air pollutants at rural sites across the UK over the past two decades on identify areas where expertise or technological limitations are likely to be a barrier to involvement of volunteers. The process of doing this will enable recognition of areas where improvement of protocols or technical kit may enable greater use of volunteers, as in the NAMN example.

Incomplete monitoring

For some monitoring activities it is of key importance that monitoring is both spatially and temporally representative. For example, Countryside Survey (CS) provides information at a national level, for specific time intervals. CS is a labour intensive survey where multiple measurements are taken across GB 1km squares, some of which are remote and not easily accessible. Failure to collect data of a consistent quality from all sites during the specific survey years would have significant impacts on the statistical validity and representativeness of the data collected. The use of paid trained scientific staff ensures that all data are collected at all squares at the appropriate time. For monitoring schemes exclusively carried out by volunteers incomplete monitoring can take a number of forms:

Geographic – remote and unpopulated areas as well as areas perceived as 'less interesting' will be less well represented in the sample. This can be countered e.g. the NAMN pays an honorarium for collection from remote sites.

Temporal – datasets become more valuable with time but discontinuities in data collection can be problematic. Consistent regular monitoring can be particularly useful in situations where evidence is needed fast, e.g. In 2010 the Environmental Change Network[24] provided evidence from monitored vegetation plots to the UK Government to determine that chemical deposition from the Icelandic volcanic eruption would not cause health problems for cattle.

Species/Science area – some areas of science attract more volunteers than others. For example bird monitoring is popular and can be coordinated and quality assured[25] largely be-u-16(m-96(b)-6(r)i94(a)o)7(o)-7(f)13(9)-16(e)4(p96(b)-6(rt)13(98Td[v)7(o)-65u)-8

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I am happy to report another successful meeting, jointly hosted by SoBRA and the RSC Toxicology group. The De-

The First UK Solar to Fuels Symposium (see http://www.rsc.org/ConferencesAndEvents/RSCConferences/Solar/index.as) was organised by the Environment, Sustainability and Energy Division (ESED) with the support of the Dalton Division, the Faraday Division and the Materials Chemistry Division; it was also sponsored by RSC Publishing under the auspices of the journal Energy and Environmental Science. The aim of the one-day symposium was to provide an opportunity for the growing interdisciplinary UK solar-to-fuels research community to address the challenges of using sunlight to drive the synthesis of molecular fuels. An RSC report of the research area, “Solar Fuels and Artificial Photosynthesis: Science and Innovation to Change our Future Energy Options”, is available at www.rsc.org/solar fuel.

The importance of this topic was underlined by a brief presentation (“US Perspective on Solar to Fuels: How We Got to Where We Are”) given by Raymond Orbach (Director of the Energy Institute, University of Texas at Austin). He described a recent competition, set up by the US Department of Energy, in which institutes competed for $122 million to set up a “Sunlight Energy Innovation Hub”. The Hub was to focus on creating a prototype device to produce fuel from the sun ten times more efficiently than plants. The competition was won by the Joint Centre for Artificial Photosynthesis at Caltech (which led a consortium of Californian university and research institutions). The bidding process energised and developed the research community involved in solar to fuel.

In opening the proceedings, James Durrant (Imperial College, London) described a resurgent and expanding UK community that needed more coherence and a clear vision for sunlight to fuels technology and explained that the meeting was an attempt to establish and support such a community. Bill Rutherford (Imperial College, London) then spoke on

After lunch Robin Perutz (University of York) spoke on “A Porphyrin –

The World Meteorological Organization's Annual Statement on the Status of the Global Climate said that 2011 was the 11th warmest since records began in 1850. It confirmed preliminary findings that 2011 was the warmest year on record with a La Niña, which has a cooling influence. Globally-averaged temperatures in 2011 were estimated to be 0.40° Centigrade above the 1961-1990 annual average of 14° C.

Precipitation extremes, many of them associated with one of

Forthcoming symposium

RSC Environmental Chemistry Group, RSC Toxicology Group and IES

50th Anniversary – the lasting legacy of Rachel Carson

A one-day symposium organised by the RSC Environmental Chemistry Group, the RSC Toxicology Group and the Institution of Environmental Sciences (IES)

Where: **Chemistry Centre, Burlington House, Piccadilly, London**

When: **2nd October 2012 from 10:00 to 17:00**

Programme

Introduction – Rachael Carson's work

Rachel Carson's influence on US legislation

Toxicology case studies of environmental exposure

The changing profile of persistent organic pollutants

Bioavailability and/or environmental fate modelling

Current pesticide practice

Consequences of hazard-based regulation such as REACH

Forthcoming symposium

Health and Hydrogeology: understanding the imLJact o Ŧ ground ǿ ater on LJeoLJle

Wednesday, 7th November 2012: The Geological Society, Burlington House, Piccadilly, London

Arsenic in groundwater

Metal concentrations in the soils and native plants surrounding the old flotation tailings pond of the Copper Mining and Smelting Complex Bor (Serbia)
00ÖQMHYLü et al.
J. Environ. Monit., 2012, 14, 866-877

Arsenic contamination and speciation in surrounding waters of three old cinnabar mines
Raquel Larios et al.
J. Environ. Monit., 2012, 14, 531-542

Migration of As, Hg, Pb, and Zn in arroyo sediments from a semiarid coastal system influenced by the abandoned gold mining district at El Triunfo, Baja California Sur, Mexico
Ana Judith Marmolejo-Rodríguez et al.
J. Environ. Monit., 2011, 13, 2182-2189

Community exposure to arsenic in the Mekong river delta, Southern Vietnam
Hoang Thi Hanh et al.
J. Environ. Monit., 2011, 13, 2025-2032

Arsenic transformations in terrestrial small mammal food chains from contaminated sites in Canada
Jared R. Saunders et al.
J. Environ. Monit., 2011, 13, 1784-1792

Study of leachability and fractional alteration of arsenic and co-existing elements in stabilized contaminated sludge using a flow-through extraction system
Janya Buanuam et al.
J. Environ. Monit., 2011, 13, 1672-1677

The biogeochemistry of arsenic in a remote UK upland site: trends in rainfall and runoff, and comparisons with urban rivers
A. P. Rowland et al.
J. Environ. Monit., 2011, 13, 1255-
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J. Environ. [illegible]

Presence and partitioning properties of the flame retardants pentabromotoluene, pentabromoethylbenzene and hexabromobenzene near suspected source zones in Norway
Hans Peter H. Arp et al.
J. Environ. Monit., 2011, 13, 505-513

Evaluation of old landfills – a thermoanalytical and spectroscopic approach
Ena Smidt et al.
J. Environ. Monit., 2011, 13, 362-369

Occurrence of pesticides in surface water bodies: a critical analysis of the Italian national pesticide survey programs
Antonio Finizio et al.
J. Environ. Monit., 2011, 13, 49