PyNe

"PyNe will continue to keep you up to date with the biomass pyrolysis area."

Pyrolysis of Palm Oil Residues in Malaysia

By R.H. Venderbosch, E. Gansekoele, J.F. Florijn, D. Assink, BTG Biomass Technology Group B.V. and H.Y.Ng, Genting Bio-oil BHD

Introduction

In co-operation with the Malaysian based Genting Sanyen Bhd, BTG Biomass Technology Group BV has completed the first pyrolysis plant based on rotating cone pyrolysis technology, in which Empty Fruit Bunches (EFB) are converted into pyrolysis oil (see Figure 1).

Usually, the wet EFB (moisture content of approximately 65 wt%) are combusted on-site yielding only ash which can be recycled to the oil palm plantations. The palm-mill produces about 6 t/hr of this wet EFB, and as a new alternative to combustion, the EFB can be converted into fast pyrolysis oil. Prior to feeding it into the pyrolysis plant, the EFB is comminuted and dried to a moisture content of about 5-10%. In this way, all the wet EFB from the palm is converted into approximately 1.2 t/hr pyrolysis oil.

Figure 1: Empty Fruit Bunches (EFB).

Figure 2: The conversion unit.

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PyNe is also sponsored by IEA Bioenergy, Aston University

Figure 3: Malaysian Pyrolysis Plant.

Figure 4: Feedstock reception area.

The pyrolysis plant was designed and built within 9 months in The Netherlands by BTG and Zeton. In January 2005 the plant was shipped to Malaysia and re-assembled. From April 2005 onwards the pyrolysis plant has been extensively tested, modified and optimised. The main achievements were:

- Significant improvement in overall plant reliability, including pretreatment section.
- Production of first batches of good quality pyrolysis oil from the dry EFB.
- Significant improvement in pyrolysis oil quality, with respect to water content and ash content. A consistent oil is produced with a typical water content of about 25 wt%.

The project has now entered the final stage of commissioning.

Indications of pyrolysis investment costs range from 2 to 3 M€ for a 2 t/hr installation. This broad range of costs is a consequence of uncertainties in location, means of control, type of feedstock, etc. The highly automated plant can be operated by two (trained) persons. The electrical consumption is below 150 kWe, and principally, all this electricity can be generated by the pyrolysis gas in an appropriate gas engine. Charcoal is used to supply the heat required by the plant. Additionally, it is expected that most of the heat for the drier can also be taken from the excess heat generated in the pyrolysis system.

Any party interested in green oil are welcome to talk with either BTG or Genting Bio-oil Sdn Bhd *www.genting.com* about their specific requirements. Deliveries of varying amounts can be made, from small amounts of 10 litres up to 20 to 100 tons or more.

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New Developments in Ablative Fast Pyrolysis at PYTEC, Germany

By Dietrich Meier, BFH-Institute for Wood Chemistry, Germany; Stefan Schoell and Hannes Klaubert, PYTEC, Germany

Introduction

PYTEC Thermochemische Anlagen GmbH, Lüneburg, Germany, has installed the first fast pyrolysis plant in Germany operating with an ablative pyrolyser. Inauguration of the plant was on 4th August 2005, with the Minister for Environment of Lower Saxony; Hannover in attendance, as his office is strongly supporting the pyrolysis project. Commissioning of the plant is envisaged for October 2005. Figure 1 shows an overall view of the new PYTEC site.

Figure 1: The PYTEC site.

Figure 2: Feed bin and drum dryer.

Figure 3: Insulated disc compartment.

Figure 4: CHP plant.

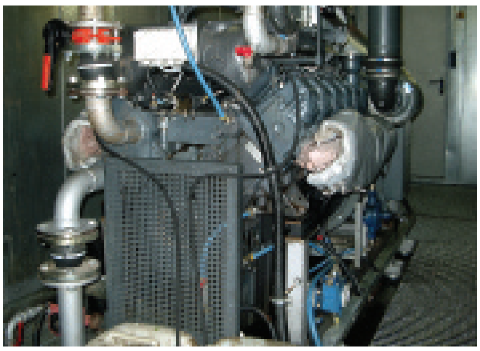

Figure 5: Mercedes Engine.

The plant is designed for 6 tonnes per day throughput of normal wood chips without prior grinding. Figure 2 shows the feed bin (blue container) and below the drum dryer. The chips fall from the top bin into the dryer and are then transported via a conveyor to the top of the pyrolyser where they enter the compactor unit. From here the chips are hydraulically pressed against a heated rotating disk which forms the heart of the plant. Figure 3 shows the insulated disc compartment. After collection and storage of the bio-oil it is burnt in the CHP plant (see Figure 4).

The special feature of the plant is that all system components are placed in standard containers in order to facilitate authorisation, transportation and assembly. The pyrolysis plant is erected at a saw mill site in Bülkau (near Cuxhaven, North Germany) which is producing roughly 100 tonnes per day of untreated waste wood chips.

An important milestone was reached by PYTEC in December 2004, when they continuously operated a modified 12 cylinder Mercedes-Benz CHP diesel engine on bio-oil for 12 hours (Figure 5). Only 4 vol.% of fossil diesel fuel was added. The bio-oil was delivered by FORTUM, Finland, and produced in their Forestera® plant. During the smooth engine operation, ca. 3 MW electricity (300-320 kWel/h) were produced and fed into the grid. No fouling of the motor parts could be observed. These results encouraged PYTEC to install the same CHP-type system at their ablative pyrolyser plant in Bülkau.

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Catalytic hydrogenation of bio-oil for chemicals and fuels

By Douglas C. Elliott, Pacific Northwest National Laboratory, Richland, Washington, USA

Figure 1: Bench-scale catalytic hydrotreater system for bio-oil.

Project Summary:

Utilising the expertise developed in the earlier work, the research in this area since 2003 has involved testing innovative metal catalysts designed for use with the high-moisture environment of bio-oil. The combination of these catalysts with processing conditions better suited to bio-oil has led to new product slates through upgrading both whole bio-oil (from different biomasses and biorefinery residue, i.e. bagasse) and bio-oil fractions, such as pyrolytic lignin. Specifically, the project involves the process development of enabling technology for catalytic hydrogenation for converting bio-oil to value-added products. Basic chemistry studies are underway in bench-scale reactor systems to better understand catalytic effects on chemical mechanisms and kinetics for upgrading. Initial results have identified product fractions, which have value as chemical products, e.g. cyclohexanols and phenolics. In some cases, the product slates have properties more applicable to conventional petroleum refining operations. Specifically, such products were tested and found to be useful feedstock in conventional hydrocracking technology for production of hydrocarbon product streams.

Project Strategy:

The scope of work includes optimising processing conditions and demonstrating catalyst lifetime for catalyst formulations that are readily scaleable to commercial operations. We use a bench-scale, continuous-flow, packed-bed, catalytic, tubular reactor, which can be operated in the range of 100-400 mL/hr., from 50-400°C and up to 20MPa (see Figure 1).

With this unit we produce upgraded bio-oil from whole bio-oil or useful bio-oil fractions, specifically pyrolytic lignin. The product oils are fractionated, for example by distillation, for recovery of chemical product streams. Other products from our tests have been used in further testing in petroleum refining technology at UOP and fractionation for product recovery in our own lab. Further scale-up of the technology is envisioned and we will carry out or support process design efforts with industrial partners, such as UOP.

Recent Accomplishments:

A better understanding has been developed of the properties of current bio-oil products as produced with various catalyst metals over a range of processing conditions. Earlier process chemistry modelling carried out in batch reactor demonstrated some of that chemistry[1]. The experiments in the continuous-flow catalytic reactor system have since verified those results. The products are being analysed by gas chromatography with mass spectrometric detector (GC-MS) and a flame ionisation detector (GC-FID), as well as carbon-13 nuclear magnetic resonance (NMR) analysis.

Future Plans:

In line with the support of the U.S. Department of Energy for the bio-refinery concept, evaluations will be carried out of new catalyst formulations and processing conditions for efficient conversion of bio-oil to value-added products. Catalyst lifetime issues will also be investigated. Sufficient hydrogenated product is generated so that product tests can be performed, including any required separation and purification.

Important reactions identified include:

- hydroxyacetaldehyde ➢ ethylene glycol
- acetol ➢ propylene glycol
- acetic acid ➢ ethanol
- furfural ➢ tetrahydrofuran-methanol
- methyl-hydroxy-cyclopentenone ➢ methyl-cyclopentanone ➢ methyl-cyclopentane
- isoeugenol and eugenol ➢ 4-propyl-guaiacol
- acetovanillone ➢ ethyl-guaiacol
- alkyl-(propyl, methyl, and ethyl) guaiacols ➢ alkyl-methoxy-cyclohexanols ➢ alkyl-cyclohexanols or to alkyl-phenols ➢ alkyl-cyclohexanes
- oleic acid ➢ stearic acid ➢ heptadecane

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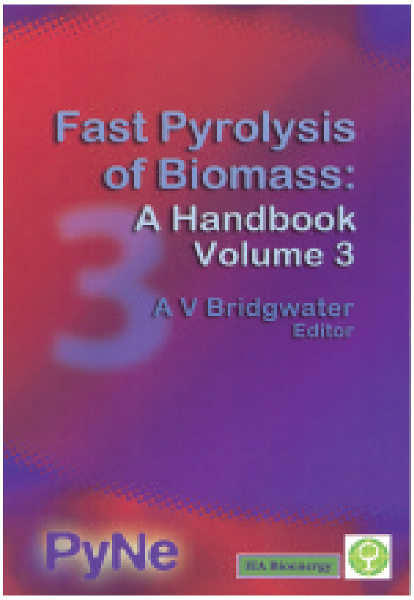
[1]Elliott, D.C.; Neuenschwander, G.G.; Hart, T.R.; Hu, J.; Solana, A.E.; Cao, C. 2005. "Hydrogenation of Bio-Oil for Chemical and Fuel Production." In: Science in Thermal and Chemical Biomass Conversion, A. V. Bridgwater and D. G. B. Boocock, eds., Blackie Academic & Professional, London, in press.

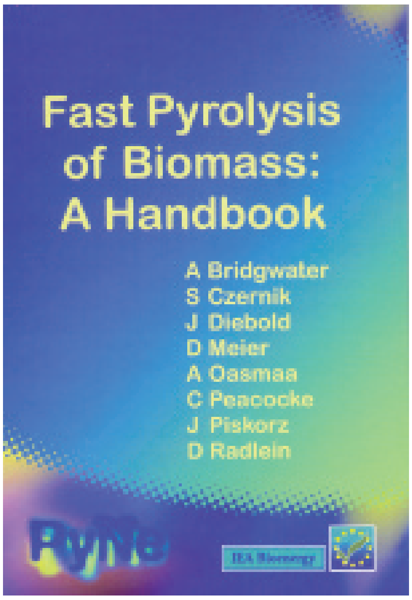
Fast Pyrolysis of Biomass: A Handbook Volume 3

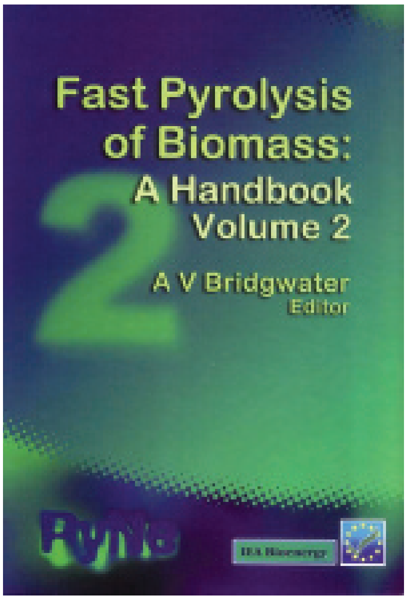


The third volume in the PyNe series is now available. This handbook provides a companion volume to the first and second handbooks and contains the following chapters:

1. The Pyrolysis Network PyNe.
2. Determination of Norms and Standards for Bio-oil as an alternative renewable fuel for electricity and heat production.
3. Characterisation, Analysis, Norms & Standards.
4. Environment, Health and Safety Aspects Related to Pyrolysis.
5. Biodegradability of Fast Pyrolysis Oil.
6. Bio-oil Toxicity Assessment Versus Pyrolysis Parameters.
7. Applications of Biomass Fast Pyrolysis Oil.
8. Kinetics and Modelling of Biomass Pyrolysis.
9. The Science and Technology of Charcoal Production.
10. Opportunities for Bio-oil in European Heat and Power Markets.
11. Technical and Non-Technical Barriers for Implementation of Fast Pyrolysis Technologies.
12. Policies and Strategies for Fast Pyrolysis.

The first two volumes are also still available:





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Environmental Enhancement through Cornstover Utilisation

By Robert C. Brown, Iowa State University, USA

Iowa State University is leading a research consortium to develop a pyrolysis-based system that employs Cornstover for production of a nitrogen-rich, biologically active char that both enriches the soil and sequesters carbon from the atmosphere.

Cornstover - the part of a corn crop remaining in the field after harvest - is one of the largest biomass resources in the United States that could be marshalled into early service as feedstock for the production of bio-based products. The potential supply of this fibrous biomass in the United States is between 75 million and 230 million dry tons per year, depending on the intensity of crop production.[1] Opinion is divided on exploiting this resource since corn tillage requires intensive use of inorganic fertilisers and some fraction of uncollected stover contributes to soil carbon.[2] The proposed fibre-to-fertiliser system would address these concerns by providing a renewable source of energy for production of nitrogen fertiliser while building soil carbon.

Process

In this system concept, illustrated in Figure 1. Cornstover, or other fibred-rich agricultural residues, is collected and pyrolysed to yield fine, porous char (Figure 2) and energy-rich bio-oil (Figure 3). The bio-oil, which can be thought of as densified biomass, is transported by tanker truck to a central facility for steam reforming to hydrogen,[3] followed by some part of it being converted to anhydrous ammonia (the process yields excess hydrogen for other applications). Using existing infrastructure of the agricultural fertiliser industry, anhydrous ammonia is transported back to the distributed pre-processing facilities where it is reacted with carbon dioxide, water, and char,[4] which are byproducts from pyrolysis of biomass, to yield ammonia bicarbonate (NH_4HCO_3) precipitated within the pores of the char. The nitrogen-rich char is injected into the soil where it serves three purposes: nitrogen fertiliser, biologically-active soil amendment, and a means for sequestering carbon from the atmosphere.

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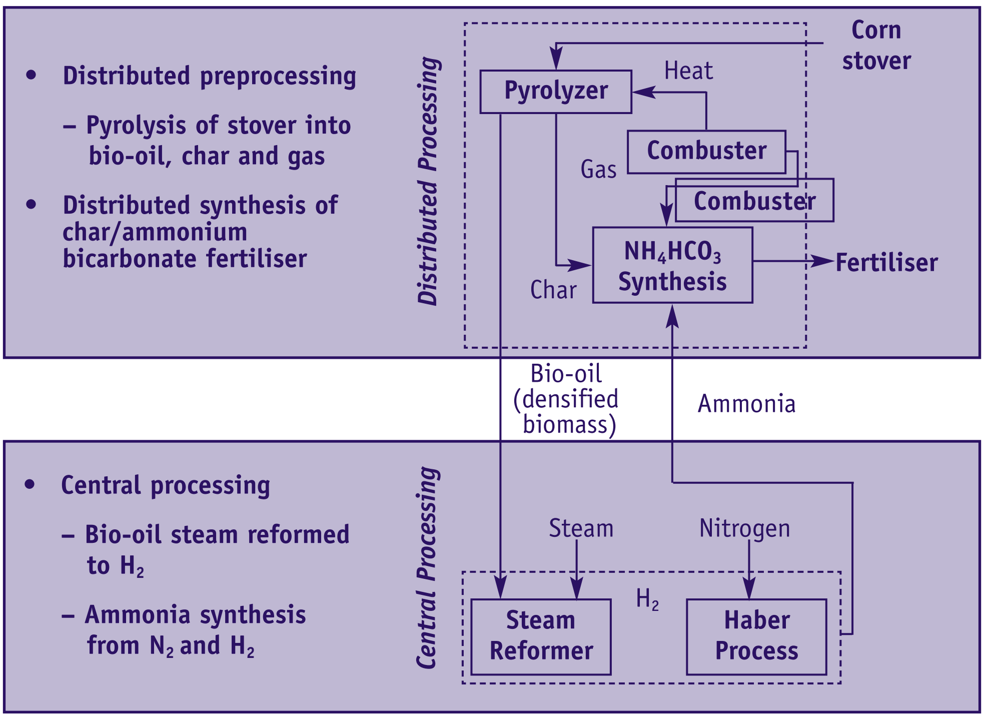

Figure 1: Cornstover Pyrolysis Process.

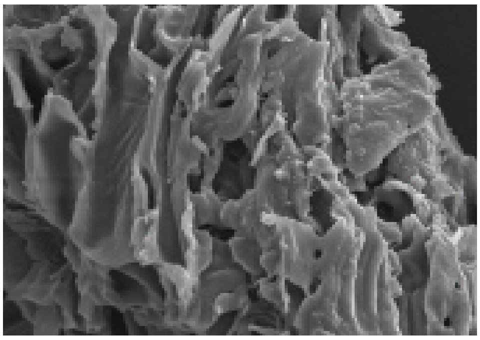

Figure 2: Porous char.

Figure 3: Energy rich bio-oil.

Background

The idea of using char to enrich soils originates from studies of Terra Preta soils in the Amazon Basin of South America.[5] These anthropogenic soils were created by the gradual addition of charcoal to the soil by pre-Columbian indigenous people. A number of investigations show these soils to have remarkably enhanced fertility compared to untreated soils in the same locations, which is thought to arise from increased biological activity within the porous char.[6] Furthermore, this carbon appears to have been stably sequestered as soil organic matter (SOM) for hundreds of years.

In this system, the farmer provides the energy to manufacture the fertiliser required for his own farm, with substantial benefits to both farmer and the environment. A 250 ha farm in corn production would save 1,000 GJ of natural gas annually by using stover to manufacture ammonia and would avoid releasing 57 t of CO_2 into the atmosphere. For supplying stover to the fertiliser manufacturer, the farmer would also receive a fuel credit equal to about 50% of the cost of anhydrous ammonia.

While switching from conventional tillage to no-till would sequester only about 280 t of carbon dioxide per year, the charcoal produced by this farm would effectively sequester 1,630 t of carbon dioxide—the annual tailpipe emissions from 330 automobiles. Although their value in the U.S. is only speculative at this time, the value of carbon credits in international markets averages about $3.50/t, or about $6,650 for a 250 ha farm.

Project

The team assembled for this investigation includes Iowa State University, National Renewable Energy Laboratory, Oak Ridge National Laboratory, the USDA ARS North Central Soil Conservation Research Laboratory, Cargill Corporation, and Eprida, Inc. The goals of this project include controlling pyrolysis conditions to achieve optimum mass fractions of bio-oil, char, and gas for production of fertiliser; improving steam reforming of bio-oil to obtain hydrogen for synthesis of anhydrous ammonia; synthesising ammonium bicarbonate-impregnated char with desirable agronomic properties; establishing the carbon sequestration potential of the proposed N-rich char fertiliser; evaluating the corn yield response to the application of different amounts of nitrogen-char fertiliser to soils; and evaluating the economic performance of the proposed fertiliser system.

The U.S. Department of Agriculture recently announced its intent to support this work as a three year project (http://www.usda.gov/wps/portal/!ut/p/_s.7_0_A/7_0_10B?contentidonly=true&contentid=2005/10/0426.xml). Additional support comes from the Iowa Energy Center and Iowa State University.

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Biotox – Bio-oil Toxicity Assessment

By Joel Blin & Philippe Girard, Cirad, France

Objectives

The project has screened a total of 21 bio-oils from a wide variety of technologies, feedstocks and production conditions for their impact on the environment and on humans. A representative oil was then subjected to a comprehensive assessment of the toxicity and eco-toxicity in order to compile a dossier for formal notification and an authoritative MSDS.

Samples screened

Samples were produced from different pyrolysis reactors (fluid bed, rotating cone, circulating fluid bed, ablative pyrolysis, vacuum pyrolysis, slow pyrolysis), under different temperature conditions (450 to 600°C), and from different biomass types (forest residues, wood chips, energy crops). These bio-oils were then chemically and physically characterised and their biodegradability and evaluation of toxicity were assessed in screening tests.

Based on the screening tests results, a suitable bio-oil sample was selected for a complete set of toxicological and eco-toxicological analysis, which is still ongoing. Results of these mandatory tests, required by the EU legal authorities, were used to draw up the MSDS safety procedure and guidelines for bio-oils usage and transport preparation, as well as recommendations on the best operating conditions to be used to obtain environmentally friendly products.

Screening tests

Details of all analytical tests performed on the fourteen bio-oils are summarised in Table 1.

Table 1 – Analytical tests carried out on bio-oils.

Type of study	Detailed analysis
Physico chemical	Chemical composition
	Viscosity (at 20 & 50°C)
	pH
	Density
	Stability
	Solids content
	Water insoluble content
	PAH
	Elemental Analysis C,H,N & O
Toxicological	Bacterial reverse mutation test
Eco-toxicological	Algal growth inhibition test
	Acute toxicity in Daphnia Magna
Biodegradability study	Modified Sturm test

Results of the physicochemical tests

Most of the oils showed typical characteristics of fast pyrolysis liquids: the water contents were in the range of 22 to 30%; density was around the normal value of 1.2 gcm^{-1}; the solid content varied between 0.03 to 2.5%.

The gas chromatographic results show that a maximum of 28.7 wt% of the whole bio-oil could be identified by GC corresponding to 70-80% of the total GC-peak area. The identified single components were clustered into different chemical groups (see Figure 1 overleaf), of which acids, phenols, and sugars dominated. The variation of these groups within the oils is quite substantial and reflects the different processing parameters such as pyrolysis techniques and condensation modes.

The oils produced with the longest vapour residence times, exhibit the highest PAH values. The same is true for fractionated vacuum pyrolysis oil. The latter has the highest PAH content of 104 ppm. The other PAH levels vary between 23 and 3 ppm. The reason for the large variation is not yet clear, but it appears that temperatures higher and lower than 500°C tend to give high PAH concentration.

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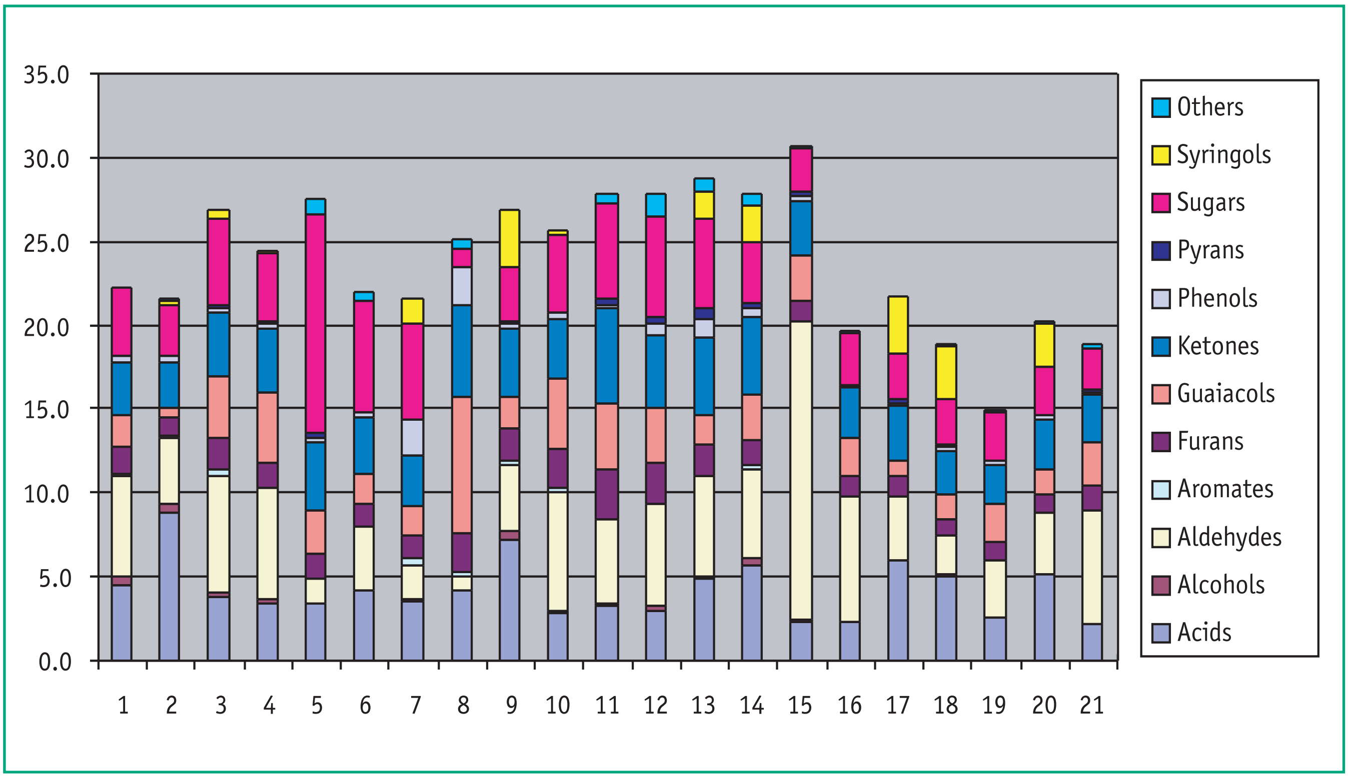

Figure 1: Distribution of chemical groups in the bio-oils (wt.% based on wet oil).

Results of the Toxicological tests

All toxicological and eco-toxicological were carried out on the water soluble components of the samples provided.

An Ames test for mutagenicity was carried out for all the bio-oils using five strains of bacteria. In all cases, there was at least one test for a Salmonella typhimurium strain where the increase in number of revertants reached the level specified in international regulations to be considered as a positive mutagenic result. Based on these results all bio-oils must be considered to be mutagenic.

Results of the Eco-toxicological screening tests

The toxicity of bio-oil to daphnia magna was studied, and showed that bio-oils have a weak or nil eco-toxicological effect. The Algal growth inhibition study demonstrated a very rare effect of fast pyrolysis oils on the unicellular green algal: low concentrations of bio-oils in the medium had a fertiliser effect, increasing algal growth, and high concentrations of bio-oils induced an inhibition of algal growth. The Acute toxicity in daphnia magna study demonstrates that bio-oils have no toxicological effect on small animals.

Complete set of toxicological and eco-toxicological tests

Based on the screening tests results and the experience of the partners, the following parameters were selected to produce the representative sample for the full toxicological and eco-toxicological tests:

- A temperature of 500°C : based on the results of the chemical analysis which determined the best pyrolysis temperature around 500°C to minimise the PAH level
- Spruce feedstock: soft wood is a typical European biomass
- Fluidised bed process: this is the common industrial process used for bio-oil production.

The necessary full toxicological and eco-toxicological tests for notification are currently being finalised by CIT and are listed in Table 2 (on next page).

Table 2 – Full toxicological and eco-toxicological tests.

Study title
Physico-chemical properties
A6 / Water solubility
A8 / Estimation of the partition coefficient
A14 / Explosive properties
Toxicological studies
B1 tris / Oral route - rat
B3 / Cutaneous - rat
B4 / Cutaneous - rabbit
B5 / Eye irritation - rabbit
B6 / LLNA
TSR / 7-day study oral route in rats
MAS / Micronucleus test in vivo
MNV / Micronucleus test in vitro
Eco-toxicological study
C2 / Acute toxicity in daphnia magna

Outcomes

- The results of the full characterisation of the bio-oil are to be used to establish a definitive Materials Safety Data Sheet (MSDS) and to set up the dossier which could be used to complete a dossier for a future full notification under REACH.
- This MSDS sheet will be published on the PyNe website (www.pyne.co.uk)
- Fast pyrolysis bio-oils appear to offer no eco-toxicological effects
- Fast pyrolysis oils appear to have a slight mutagenic effect, but appear overall to be less harmful than conventional diesel fuel.
- The detailed biodegradability results will be published in the next issue of PyNe.
- Protocols used for these tests, full results, and the dossier for notification will be available shortly on the PyNe Website
- This project has been conducted with the EU support and through support from all bio-oil producers.

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Advances in Dry Distillation Technology

By Peter Fransham, Advanced Biorefinery Inc., Canada

Background

Advanced BioRefinery Inc. (ABRI) is the new name for the former Encon Enterprises Inc. In the late 1980's and early 90's Encon experimented with fluidised bed pyrolysis systems. A 200 kg/hr mobile pyrolysis unit was constructed on a standard drop deck trailer with the intention of converting Newfoundland peat moss to liquid fuels.
The system was tested extensively until 1994 when it became evident that design limitations precluded the scale-up to a commercial size. In 1994, Encon started working with heated augers to drive off wood preservatives from salvaged utility poles. A bench scale unit was built and tested with positive results. While it is possible to drive off volatile matter with a hot shell auger, scale-up becomes impractical on account of heat transfer limitations through the auger shell. Perhaps the most impressive outcome of the experiments was the potential recovery of upwards of 60% by weight of quality bio-liquid at reactor temperatures around 400°C.

Continued overleaf...

Process development

To overcome energy transfer limitations through the auger shell, a hot, high-density heat carrier is mixed with the biomass in the mixing auger. The volatile matter is rapidly driven off and immediately condensed. The system is therefore inherently different from sand transport bed and fluid bed reactors in that the hot vapours are rapidly removed from the char. Bench scale testing has shown that all of the volatile matter can be efficiently driven off from the biomass at approximately 380ºC. The lower reactor temperature also limits secondary reactions prior to condensation. No sweep gas is required thereby eliminating the need for large blowers to move the sand heat carrier.

The system has wide turndown capabilities and can operate over a range of temperature and residence time. The overall system is greatly simplified and overall capital costs are significantly reduced.

Figure 1: One tonne per day mobile pyrolysis unit.

Current status

ABRI has evolved since the early days of fluid bed technology. A 5 dry tonne per day (dtpd) mobile system has been constructed and is operational at a large chicken farm in Alabama. A 15 dtpd plant is waiting for permission to be completed and will be set up at a saw mill in Massachusetts. ABRI has departed from conventional thinking that big is better and is presently commissioning its 1 dtpd system for on-farm use. Figure 1 shows the system complete with a chain flail dryer and pyrolysis system. The option to burn char in a furnace has been included. Currently the process gas is flared, but ultimately ABRI plans to use to gas to provide the necessary electricity to run the plant. The char provides the necessary heat for drying and conversion. More char is produced than is required for the process and work is underway to concentrate nitrogen in the char and provide a viable fertiliser. Poultry feed contains fat and therefore the liquid produced has a higher calorific value than woody biomass. A boiler is presently being designed and constructed to burn the bio-liquids and provide heat for the poultry barns. Natural Resources Canada and Agriculture Canada are providing funding for this project.

ABRI is also constructing a transportable 50 dtpd plant for onsite management of logging wastes. The plant is made up of seven skids and can be transported to the biomass. The 50 dtpd plant is slated for shakedown testing during the second quarter of 2006 and will likely see service in the field sometime later in the summer. The bio-liquids will be shipped to a pulp and paper mill and will be used to offset combustion of expensive natural gas. Ontario Ministry of Natural Resources and industrial partners are funding this three year pilot study as part of an overall effort by the Ontario Government to increase the utilisation of forest resources.

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The Renewgen Systems Inc. Process

By Sam Ahad, Renewgen, Canada

The Renewgen process is the miniaturisation, optimisation and computer control of a wood charcoal based biorefinery. This low temperature pyrolysis of wood (such as slash, SDU (Small Diameter Underutilised) and pine beetle infested) is a continuous process. It can yield up to 33% of wood charcoal for fuel and activated carbon. Much more importantly, the process can yield significant amounts of methanol, acetic acid and tars.

Up to now, most wood charcoal manufacturing processes in forestry clear cuts have either utilised the product gas stream as fuel for the carbonisation process or flared it. Only large and centralised wood charcoal process plants are designed to utilise the product gas stream for further processing.
The innovation of the Renewgen process is the utilisation of the product gas to dry incoming feed as well as to collect and store the gas from several skid-based portable processes in a typical forestry clearcut. The gas can be delivered to a central processing plant for conversion and/or recovery to yield methanol, acetic acid and other fractions.

In a typical forestry clear cut, the slash and other undesirable biomass, such as SDU or pine beetle infested timber is left to dry and then burnt in piles. This slashburning process is a pre-requisite step to silviculture and regulatory forest fire prevention measures. Silviculture is itself a pre-requisite step to forestry road de-commissioning and stream and wetland rehabilitation. The field based portable wood charcoal bio-refinery not only speeds up several stages in forest harvesting practices, but also yields valuable products.

Renewgen has initiated evaluation of the Lurgi methanol to propylene process (a building block with 6% annual increase in demand). In addition, Renewgen is currently evaluating the Lambiotte & Cie SA processes that develop a set of products from methanol to formaldehyde which leads to a family of acetal solvents and eventually aerosols, cosmetics and resins.

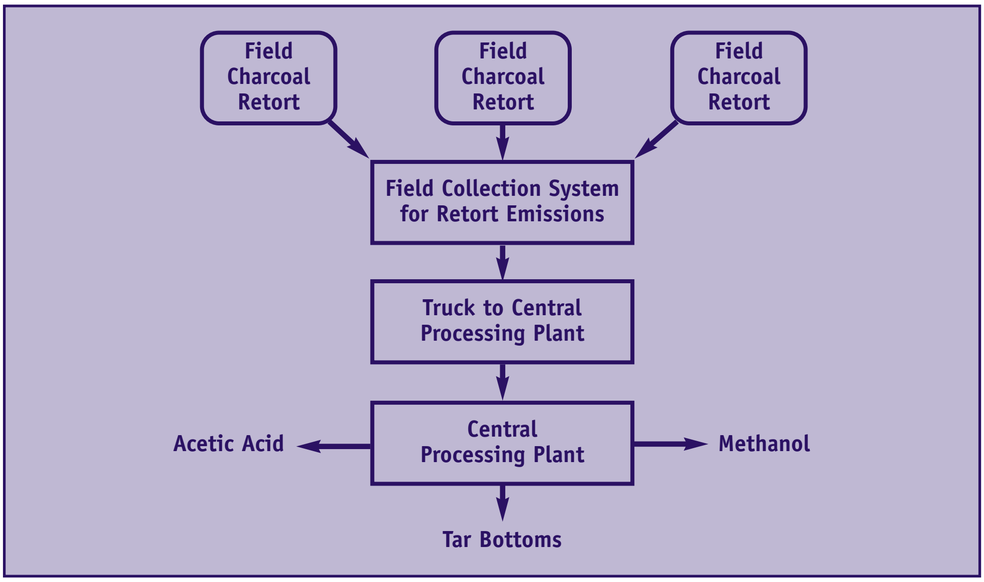

Figure 1: Renewgen process concept.

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