PyNe

Examples of Biomass Utilisation in South Africa – Application of Slow Pyrolysis

By Dagmar Honsbein, Aston University, UK

Background

Since the new South African government was formed in 1994, a "whole-tree-utilisation" approach, coupled with silvicultural principals, has been developed to replace the traditional selective usage with discarding of the residues. Up to the 1990s, the direct combustion of wood waste has been utilised as an energy source in downstream industrial activities in only a few cases in South Africa. Apart from limited production of "heat logs" from compressed sawdust and wood pellets, millions of tons of woody biomass still go to waste annually! A rough estimate (through personal discussions with various governmental institutions in South Africa) suggests that the waste is around six million tonnes annually.

To reduce wastage of raw materials in general, and particularly wastes from wood, the only renewable resource, the South African Department of Water Affairs and Forestry introduced the concept of complete utilisation of renewable resources. This also included the partial to full eradication of alien flora to South Africa in the late 1990s. One of the programmes introduced was "Working for Water", under the leadership of the Department of Water Affairs and Forestry and the Department of Environment and Tourism.

The South African Government is trying to:

- increase economic growth in South Africa in general

- satisfy the environmental standards set for future sustainable economic development (for example ISO 14000 and Clean Development Mechanism), by helping to restore ecological balances and countering environmental threats, making this an avenue for potential trades in CO_2 credits

- create employment and alleviate poverty

- increase value addition to natural, sustainable resources

- promote and facilitate an increase in productivity, quality of products, know-how and technology transfer to economic sectors that traditionally employ limited technology and standards, notably the optimal utilisation of forest resources.

Biomass Utilisation in a Slow Pyrolysis Process in South Africa

In consideration of the above issues and with the enthusiastic encouragement and support of the Department of Energy in South Africa, opportunities have been sought to add value to these primary biomass raw materials by establishing downstream industries that exploit these opportunities.

An example that is used to illustrate these policies is the Rodim Wood Chemicals cc slow pyrolysis process in South Africa. Numerous kiln processes for the primary production of charcoal still exist in South Africa. The charcoal produced as well as briquettes from the fines, is mainly sold for barbecue purposes in South Africa, Germany and the UK. A sizeable amount is also used in the silicon industry. The kilns, based on direct combustion, are usually batch and do not recover the gas produced during a production cycle. Forest waste materials and thinnings within a specific size range are mostly used to produce kiln charcoal.

A South African registered company, Rodim Wood Chemicals cc, has built on the research and knowledge accumulated over some 20 years. Rodim Wood Chemicals cc owns the only known South African slow pyrolysis process, shown in Figure 2. The slow pyrolysis system employed is based on well-documented wood pyrolysis principles. The main objective of the plant currently is to produce high quality charcoal for use in metallurgical processes in South Africa.

Figure 1: Map of South Africa

Figure 2: RWC's Slow Pyrolysis facility

The production of charcoal and other by-products is drawn from a wood distillation or carbonisation plant with a relatively low capital investment, making use of wood-based biomass waste, which would otherwise be declared as unrecoverable waste, and non-useable in kiln processes. This wood waste is sourced from sawmills, plantation-felling waste and forest thinnings within a 50km radius of the plant.

Continuous to semi-continuous slow pyrolysis is achieved by heating the woody biomass (mainly Acacia mearnsii – wattle, Eucalyptus spp, and Pine species) with a feed gas at a temperature of 600 to 700°C in an oxygen free environment. Off-gases are condensed and non-condensable gases are re-circulated to a heat exchanger for complete combustion that in turn heats the feed gas for the process. The production capacity of this plant is approximately 600 lt. of charcoal in 30 to 40 minutes depending on the moisture content and species of the feedstock to be carbonised. The primary products obtained from the process are charcoal at a yield of 33 to 40 wt.%, with a fixed carbon content at 88 to 92 per cent; ash content of around 2 to 3 per cent; and liquids in the form of wood-oils and wood-acids (light and heavy pyrolysis liquids). The products are obtained in approximately equal proportions, but no formal mass balance has been carried out on the plant.

This pyrolysis process technology is of local origin and has been well defined and is comparable to the technology used in the Reichert Retort process. Similar plants are operational in Namibia with further installations to follow in Zambia and Zimbabwe. The plants currently in operation are manned by non-skilled or low skill workers. As experience and skills grow, it is anticipated that technologies will become more sophisticated and fast pyrolysis could be introduced to maximise the production of wood-oil for energy or other relevant purposes. The production facilities fully comply with the environmental standards set by the Government of South Africa. Sampling of the air found that no poisonous liquids or gases, nor increased CO or CO_2 emissions are registered within 1 - 2 or more kilometres from the plant.

Although not many markets for the liquid products have been found in South Africa or other neighbouring countries, the plants installed in Namibia and South Africa have already been proven to be economically viable for the above-mentioned reasons. Promising markets exist for using the liquids as a fertiliser and soil-conditioning component (patent pending), and as a wood preservative as shown in Figure 3 (see overleaf). The South African Department of Minerals and Energy are fully aware of Rodim's initiative and support its endeavours.

Continued overleaf.

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Conclusion

The initial idea of setting up a semi-continuous plant was to achieve optimal utilisation of the off gases produced during the process for example by reducing drying time of wood in the process, optimising wood to products ratio and eventually to connect a power generator to the plant to use the surplus gas which is currently flared off. This idea was, however, postponed due to financial constraints at Rodim Wood Chemicals, which originated from a lack of policies for independent power producers, particularly the absence of policy frameworks or regulations, which could guarantee feeding independently produced power into the national grid.

As a result, Rodim Wood Chemicals has decided to sell production facility rights to interested entrepreneurs in South Africa, Zambia and Zimbabwe. Furthermore, the operation of the plant set up by Rodim Wood Chemicals has been leased to the foreman of the plant on a medium term contract. The charcoal and liquids are marketed through Rodim Wood Chemicals.

Figure 3: Preservative tests using slow pyrolysis liquid that have been running for more than two years (left pole treated with pyrolytic material from RWC's plant)

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Fast Pyrolysis of Biomass in a Circulating Fluidised Bed (CFB)

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Introduction

Biomass is widely viewed as the renewable energy source with the highest potential with biomass pyrolysis offering considerable potential [1, 2]. Kinetics, reaction modelling and reactor hydrodynamics have been studied. High oil yields require a very fast particle heating; a reaction temperature of ~500°C; short residence times and fast char separation and vapour condensation to avoid secondary cracking. While fluidised bed reactors can meet these requirements, only a circulating fluid bed (CFB) can achieve a short, controllable residence time.

Kinetics and Endothermicity [3]

The endothermic heat was measured by differential scanning calorimetry as between 210 kJ kg^{-1} for eucalyptus and 430 kJ kg^{-1} for sawdust. The pyrolysis kinetics were measured by TGA and demonstrated a 1st order reaction in respect of biomass with an Arrhenius-type reaction rate constant (k), defined by the activation energy (E_a) and the pre-exponential factor (A). E_a depends on the biomass type and A depends on the heating rate, which should exceed 100 K/min. Values of k at 500°C (Table 1) mostly exceed 0.5 s^{-1}: therefore a high conversion can be achieved in short reaction times, thereby limiting secondary reactions.

Table 1: Kinetic constants, E_a, A and $k_{500°C}$ (determined at 100 K/min).

Sample	E_a, kJ/mol	A (s^{-1})	k (s^{-1})
Spruce	68.4	$3.47.10^4$	0.824
Eucalyptus	86.4	$1.06.10^6$	1.52
Poplar	54.1	$1.00.10^3$	0.219
Sawdust	75.8	$9.12.10^4$	0.684
Corn	77.0	$2.55.10^5$	1.59
Sunflower	63.9	$2.48.10^4$	1.19
Straw	76.3	$3.16.10^5$	2.21
Sewage sludge	45.3	$8.95.10^1$	0.078

Conversions, Bio-Oil Yield and Modelling

The pyrolysis-yields of bio-oil, gas and char were measured in a laboratory scale batch reactor and in the pilot CFB fast pyrolysis unit at CRES, Athens. Both experiments were performed in the same temperature range. Figure 1 depicts the experimental oil-yields, literature data and model predictions. All results show the same trend and the same yield of bio-oil with a maximum (60 – 65 wt%) around 500°C.

To model the reaction, the Waterloo concept [4], with primary and secondary reactions is used, but without secondary char formation, as this has been found to be irrelevant from TGA experiments. The reactions follow the continuous reaction model with a 1st order reaction rate [3]. The reaction time can be accurately controlled by operating the CFB in plug flow mode (see below) with a uniform residence time of all particles. Small particles (< 300 µm) are used so that the internal thermal resistance is negligible [3]. The temperature is nearly constant in the reaction zone and a high heat transfer almost instantaneously heats the biomass particles to bed temperature. Secondary reactions are suppressed by short residence times.
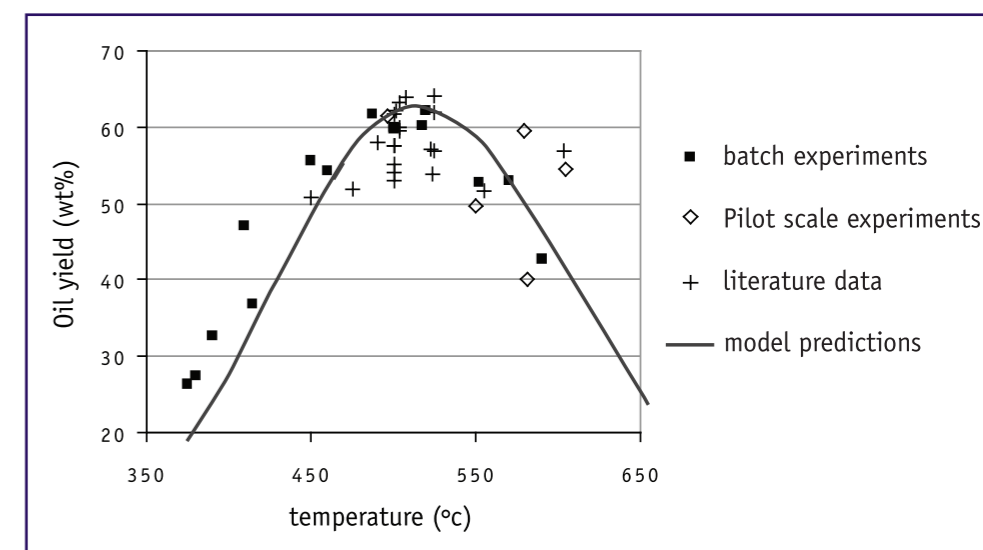
Figure 1. Bio-oil yield, own experiments, literature data and model predictions.

Table 2: Relevant model predictions for various types of biomass.

	Optimum Temperature (°C)	Oil yield (wt%), at			
		Optimum	400°C	500°C	600°C
Spruce	520	62.5	27.1	61.6	43.4
Eucalyptus	480	71.2	46.5	70.1	55.0
Sawdust	490	74.7	47.7	74.5	59.2
Corn	510	55.8	29.1	55.9	46.2
Sunflower	420	59.2	58.8	56.3	45.4
Straw	490	65.8	42.3	65.4	51.5
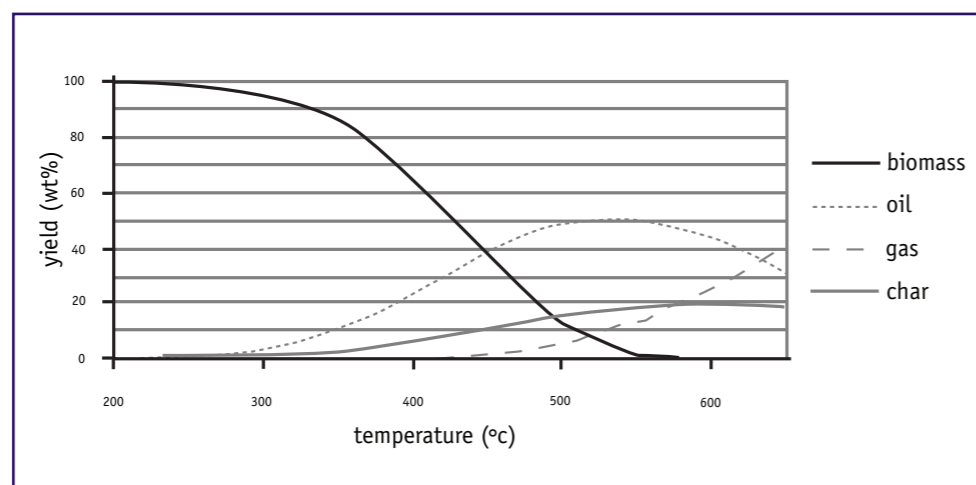
Figure 2: Model predictions of converted spruce and formed products.

The conversion equations define the fractions of bio-oil, gas and char, calculated from the residence time [5, 6] and the different kinetic constants, either measured or taken from Di Blasi [7] for the primary and secondary gas formation. The relevant overall results are presented in Table 2, and given as the oil yield at different temperatures and at the temperature of optimum yield. The model results shown in Figure 2 illustrate the conversion of spruce at a residence time of 2.5 s. A similar trend is predicted for all biomass species tested. The optimum T lies between 420 and 520°C: at higher temperatures, more gas is produced by secondary reactions. Figure 1 (see previous page) compared model predictions and data and this shows fair agreement. At lower temperatures, the experimental oil yield exceeds the model values: the model uses the equilibrium char amount (at t = ∞), thus overestimating char at shorter times. Practically, the reactor will operate at the optimum T, thus making this deviation unimportant in reactor design.

Particle Movement in the Riser of a CFB

The residence time τ of biomass particles in the CFB-riser needs to be short and accurately controllable, but depends on the operating regime. Particle plug flow is the required mode since all particles then have a uniform residence time. Back-mixing should be avoided as this gives a wide residence time distribution for the particles. Previous studies [e.g. 8, 9] mostly examine low values of solids circulation rates (G ≥ 100 kg/m²s). The present research extends this range with operation from 25 to 622 kg/m²s (G) and 1 to 10 m/s for the superficial gas velocity (U). Positron Emission Particle Tracking (PEPT) [10, 11] was used to study the movement and population density of particles in the CFB-riser. The bed material was sand with an average diameter of 120 µm and a density of 2260 kg/m³. [18]F labelled tracers were sand (~ 120 µm) and radish seed (~ 500 µm), chosen to represent the behaviour of biomass in the riser. The PEPT results demonstrate that either back-mixing or plug flow strongly depend on combined values of U and G.
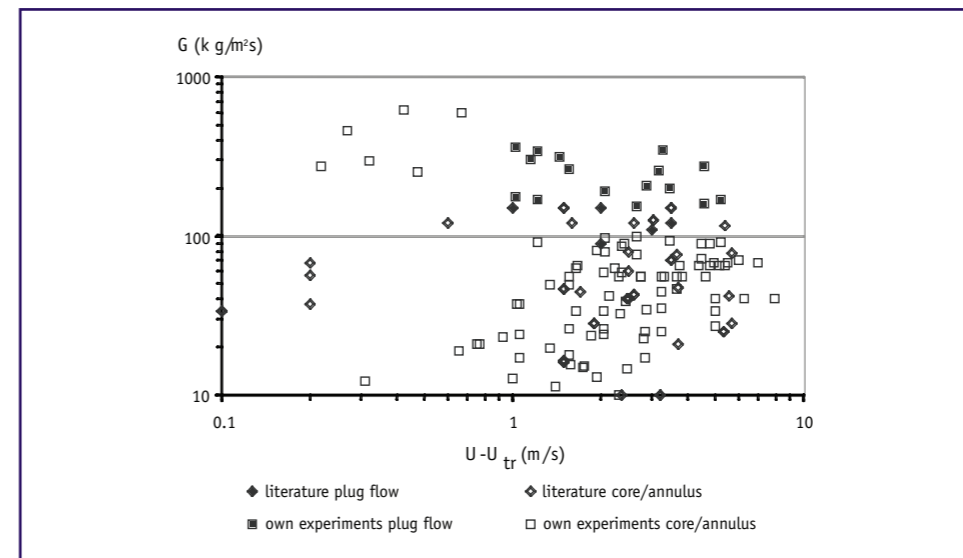

Figure 3: Plug flow and core/annulus regime in function of G and U-U$_{tr}$.

At various lower combined (U, G) values, no stable circulation in the riser could be obtained and the bed was still behaving in a bubbling or turbulent mode. A minimum superficial gas velocity (the transport velocity, U$_{tr}$) is needed to operate in the CFB-mode. This was experimentally verified [10, 11] and indicates that the equation of Bi and Grace [12] fits the experimental findings. The predicted velocity is increased by 20% as a safety measure for practical design [13].

The plots of particle movement distinguish mainly core/annulus (mixed, up and down) and plug flow (mostly up) mode. All experimental and literature data are presented in Figure 3, demonstrating that it is indicated:

(i) For operation in plug flow, as required in biomass fast pyrolysis, G needs to be greater than ~200kg/m²s and U needs to be greater than (U$_{tr}$ + 1) m/s,

(ii) For operation in mixed mode, as required for biomass combustion for example, G needs to be less than ~150 kg/m²s, irrespective of U (> U$_{tr}$). The particle slip velocity, U$_s$, is in theory U$_s$ = U/ε - U$_t$, where ε the voidage in the riser (≥ 0.98) and U$_t$ is the terminal velocity of the particle. Experimental results demonstrated that this theoretical equation only holds in the plug flow, where U$_s$ ≈ U - U$_t$, since ε is close to 1. Particle slip velocity and residence time define the required reactor height H by H = U$_s$. τ.

Final Reactor Design

The main purpose of this work is the determination of the reactor (riser) dimensions required to ensure the desired conversion. The model and reaction kinetics determines the residence time for a required oil production at a selected operating temperature (normally close to 500°C). The short residence time (a few seconds only) implies the use of small particles, practically in the range of 100-300µm, and the conversion has to be completed in a single pass through the riser. The operation of the riser is isothermal when U and G are correctly specified.

The heat balance [3, 5, 6] determines the required heat (heating of biomass and reaction heat), which can be supplied by combustion of the non-condensable pyrolysis gas either indirectly preheating the circulating bed material, or directly heating the reactor. In both cases, the combustion gas forms the nearly oxygen-free fluidisation gas. Indirect heating of the bed material separates the heat transfer and fluidisation, which simplifies the process. The char can be recovered. Operation in plug flow guarantees a constant, controllable residence time. Together with the heat balance, U and G determine the diameter of the reactor. In the plug flow mode, the slip velocity, U$_s$, equals U – U$_t$, with U$_t$ the terminal velocity of particles used as bulk bed material. The required bed height (H) is hence defined.

This design strategy is applied to a 10 MW (bio-oil) reactor, which consumes 3.4 t/hr of biomass and produces 2 t/hr of bio-oil. The riser has a diameter of 0.4 m and is 12.5 m high. The circulation rate of bed material (sand) needs to be 115 t/hr. The gas velocity should be 5.6 m/s for operation in plug flow with a residence time of 2.5 s.

An outline diagram of the complete process is given in Figure 4 (see overleaf) where different oil recovery techniques are proposed including indirect condensation, electrostatic precipitation, and combined scrubbing-condensation. The latter is recommended because of the high cost of electrostatic precipitation and the problem of preferential deposition of lignin during indirect condensation, leading to fouling of the heat exchanger surfaces.

An indicative economic evaluation of the process was made, comparing the price per GJ of bio-oil (heating value of the product) and heavy fuel oil, respectively 16 to 19 MJ/kg and around 41 MJ/kg. The required investment was estimated at 4.6 million . The average annual operating costs were 2.6 million /year for an annual production of 16320 tons of bio-oil, i.e. 158 /ton bio-oil, corresponding to 9 /GJ. If the char is sold at 46 /ton (despite its calorific advantage over coal), a reduction of 1 /GJ is achieved. The current price of heavy fuel oil is 460 /ton or 11.2 /GJ. The pyrolytic production of bio-oil is hence economically viable, even with a profit margin of 20 to 30%.
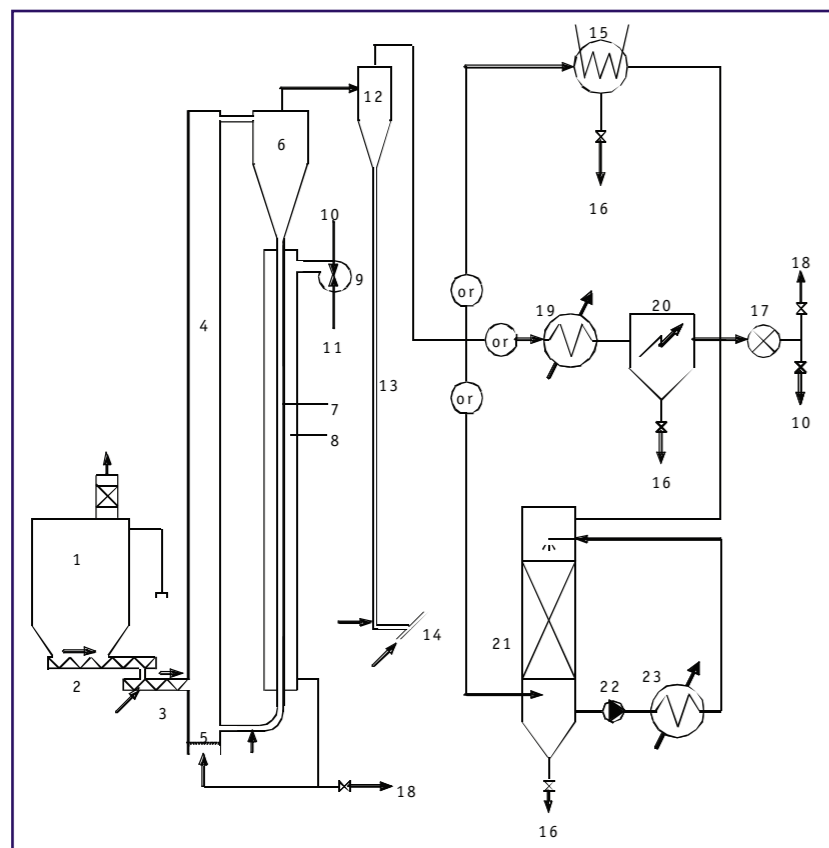
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Figure 4: Schematic diagram of the pyrolysis installation

Key:
1) biomass hopper, pneumatic feeding, baghouse filter
2) screw conveyor (variable rpm)
3) screw conveyor (high rpm)
4) riser
5) tubular distributor for combustion gas
6) low-efficiency (LE) cyclone for removing circulating bed material (sand), with cut-size 100 µm
7) downcomer and L-valve
8) radiation heater
9) burner
10) non-condensable gas
11) combustion air
12) high-efficiency (HE) cyclone for char
13) downcomer with L-valve
14) pneumatic conveying of char to silo and densification
15) condenser
16) evacuation of bio-oil
17) suction fan for non-condensable gas
18) post-combustion or flare
19) cooler
20) electrostatic precipitator
21) scrubber - condenser
22) circulation pump of bio-oil
23) cooler – heat exchanger

Conclusions

TGA experiments determined the reaction rate of pyrolysis and its Arrhenius dependency. Batch and CFB experiments yielded between 60 and 65 wt% of bio-oil at around 500°C and very short residence times of the biomass particles. A model has been developed to predict the yield of oil, gas and char as a function of operating parameters. The residence time of the biomass particles in the riser depends on the fluidisation regime. In plug flow, all particles have the required, nearly constant, residence time. Plug flow is achieved when $U \geq (U_{tr} + 1)$ m/s and $G \geq 200$ kg/m²s. A plug flow CFB of 10 MW (bio-oil) capacity requires a riser of 0.4 m I.D. and 12.5 m height. A CFB biomass pyrolysis process appears economically viable.

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Progress in the Biorefineries Task in PyNe

By Doug Elliott and Tony Bridgwater.

Definition

Consideration was given to the definition of a biorefinery, and this was defined by the PyNe group at their most recent meeting as:

A biorefinery processes and upgrades a renewable raw material (i.e. biomass) into several marketable products, emphasising fuels and chemicals.
- Marketable includes value, standards, usefulness, environmental acceptability, economics, sustainability, legislation.
- Important to consider complete use of raw material, optimisation, efficiency, effectiveness, economics, environment.

Case studies

The key contribution of PyNe will be consideration of how pyrolysis can be or should be integrated into a biorefinery. To this end, one of the outputs of the Task will be a set of case studies as summarised below:

Chemicals as primary product
- Speciality chemicals and separation.

Transport fuels as primary product
- Bio-oil for transport fuels via gasification and FT and/or methanol.
- Bio-oil (hydro)de-oxygenation for transport fuels.

Reference case
- Power and heat.

Some of the concepts that can include pyrolysis are exemplified in Figures 2 to 5 overleaf to show the diversity of biorefinery systems being considered.

Round Robin

In order to address a commonly recognized issue, a Round Robin on lignin pyrolysis has been agreed in order to consider concepts such as those illustrated in Figures 2, 3, 4 and 5 overleaf. This will be based on those laboratories who wish to participate who will be provided with a standard sample of lignin, possibly several samples if these can be resourced. Each laboratory will carry out analytical and/or laboratory scale tests and will provide full details for review and comparison. It is planned that this will result in at least one journal paper as well as a report. Lignin has been procured from several sources.

Continued overleaf.

Objective
- Compare process, methods, analyses and products to share experiences, methodologies and results.
- Publish results in a journal as a Task output.

Organisations participating
- Aston   Fundamental and Applied
- FZK   Fundamental and Applied
- ECN   Applied
- Naples   Fundamental
- Twente   Applied
- USDA   Applied
- BFH   Fundamental and Applied
- NREL   Applied
- PNNL   Applied
- VTT   Fundamental
- CIRAD   Fundamental and Applied
- IFP   Fundamental

Figure 1: PyNe Workshop

Recommendations

The last PyNe meeting also discussed and reviewed RD&D recommendations for development of biorefineries, for laboratory research, assessments and general considerations as below:

Laboratory

1. Characterisation of byproducts and wastes from current and planned biomass conversion processes

2. Find (new) uses for all byproducts and wastes from biomass conversion processes. Lignin is a good example from fermentation

3. Research into processes for production of more interesting chemical products

4. Consider appropriate separation processes, including development of new methods if necessary

5. Can new and/or modified pyrolysis or thermal decomposition technologies be developed? If so, what?

6. What upgrading and/or refining technologies need to be developed?

7. How can biomass be pretreated or modified to improve yields?

8. Use of less clean and contaminated biomass will become important, which affects process and products
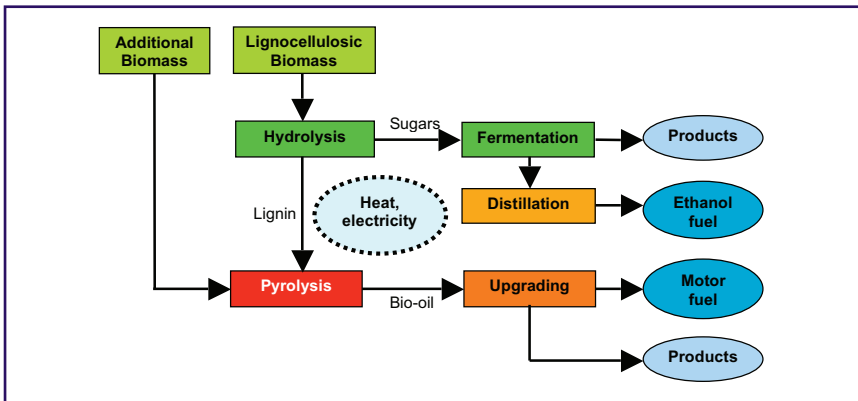
9. Feed flexible processing needed

Figure 3: Possible future biorefinery based on bio-chemical and thermochemical conversion (from 1).
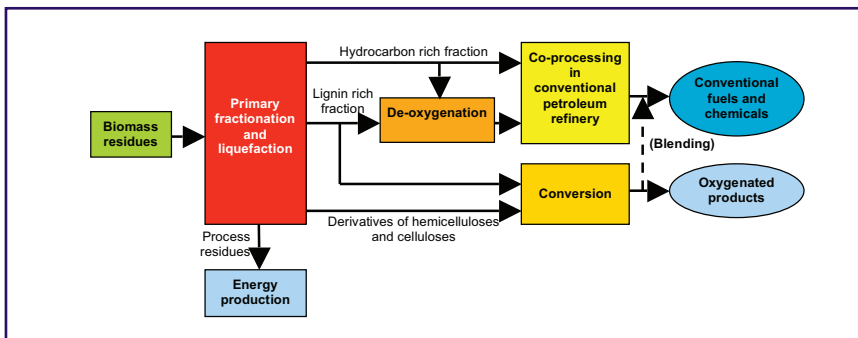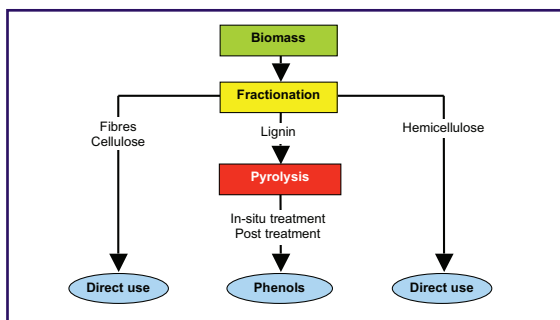

Figure 4: Overall biorefining concept (from 2).

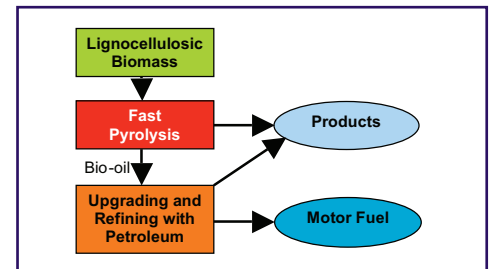*Figure 5: Biomass fractionation to support biorefining (from 3).*

Figure 2: Pyrolysis/petroleum biorefinery.

Assessment or Studies

1. Find (new) uses for all byproducts and wastes from biomass conversion processes. Lignin is a good example from fermentation.

2. Develop strategy of deciding what to produce

3. Need to match raw material, technology, product and market

4. Review products that can be produced, how they are synthesised, what they cost and compare to market opportunity

5. Evaluate raw material availability for conversion

6. Identify opportunities for specific products and groups of products

7. Build set of case studies to improve understanding of opportunities

8. How to define optimum biorefinery

9. How to identify optimum products

Considerations

1. Do not generalise too much

2. Develop feed flexible processes, including contaminated feed materials

3. Understand special limitations of a biomass economy in different locations

4. Technology transfer chemically, geographically, economically

5. There is no limitation on what can be made from biomass, only what can be made economically or competitively – so need some strategies, and need to consider time needed to become available

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