

Staged pyrolysis reactor with recovery of some valuable chemicals for agricultural and industrial use and transformation of excess heat into electricity and value added sub-products (Concept study for bio char kiln and value added CO2 capture)

The problems that are associated with the use of fossil fuels demand a transition to renewable sources for energy and materials. Biomass is a natural treasure for chemicals that up to now are made from fossil resources.

Unfortunately, the heterogeneity and complexity of biomass still preclude exploitation of its full potential. New technologies for economical valorization of biomass are under development, but cannot yet compete with petrochemical processes.

However, rising prices of fossil resources, inevitably will lead to replacement of oil refineries with bio-refineries.

A bio-refinery uses various types of biomass feed stocks that are processed via different technologies into bio char, heat, power and various liquid products. The bio-refinery is self-sustainable with respect to heat and power and puts no burden on the environment.

Thermo chemical processes such as fast or slow pyrolysis can play an important role in bio-refineries. Within the scope of biomass pyrolysis as a renewable option to produce bio-char and liquid chemicals this chapter presents a hypothetical concept of a pyrolysis-based technology that could be a potential candidate and that form the main point for the work that is described in this concept.

(De Wild PJ, Reith H, Heeres, HJ, Biomass pyrolysis for chemicals. *Biofuels*. 2 (2), 185 - 208 (2011)).

Existing biochar kilns are not well-conceived, as quality criteria for the end product or end uses are not yet established, (despite several claims from IBI and the European lawmakers etc.)

The most advanced kilns on the market to date only focus on environmental impact, cleaning up the evolving gases and liquids through burners.

Not a single biochar kiln available at the moment uses the excess energy for electricity production, the excess heat for other non-char related uses, or value added recovery of chemicals from the pyrolysis process.

To create controlled process quality, and a better economic return on fixing C in the form of biochar in soils in the future, we have to first take a more generalized look at the problem.

The whole process of transforming biomass into char and useful sub-products can be separated into several steps:

- Occurrence and handling of the raw material.
- Pre drying and sizing of the raw material
- Staged pyrolysis with recovery of sub-products
- Management/use of the heat and energy liberated in the process
- Clean up of the gases (not used to produce chemicals byproducts) as fuel for motor genset to generate electricity
- Further processing/purification of byproducts
- Transformation of the char into agronomic useful and applicable substrate, adding fertilizer, micronutrients and trace elements

Occurrence and handling of raw material

Raw material can come in any size and physical state, be it stems, branches, cuttings, roots, coppice of green material, grass, straw or manure, various sludges from industrial processes, etc. There is a wide variety of size, hardness, humidity, as well as additional contamination with soil or stones possible.

For a controlled charring process, a small, uniform size is desirable, where the particles have the same thickness over the whole extension of the particle and where the thickness itself does not exceed 5 to 8 mm.

A small, uniform size will lower the needed exposure time to the desired temperature, and the degassing of particles would be consistent and homogenized.

Overexposure in time and temperature are avoided, and applied temperature spread is small, as the core of the particle would have the same temperature and exposure time as the particle surface.

Pre-drying and sizing of the raw material

With the size and form of the particles we should as well take into account that circulating hot gases used to heat raw material to pyrolysis temperatures need sufficient surface contact to transmit heat to the particle, and evolving gases need sufficient space to be extracted in a reasonable time span.

If the particle size is sufficiently small and all particles have the same temperature, re-condensation on colder particles is avoided.

Fines below 1 mm diameter should be avoided because their exposure time would be too long and therefore the losses from the raw material stage into char too high.

The sizing or milling of the feedstock can be done in a separate operation or in an integrated mill at the feeding inlet or on top of the feeding hopper in the charring equipment or inside the charring loop.

As raw materials come with different humidity, after sizing, the particles have to be dried. In the drying stage some materials like special grasses or pines give off terpenes and other valuable volatiles, aromatic substances that should be extracted using a separate condenser. (di-terpens, tri-terpens etc.)

This kiln design would for example be perfect to char spices like rosemary, thymine, cumin, etc., because after extracting the volatile oils and terpenes in the drying /extraction step, the remaining biomass would be further heated and charred.

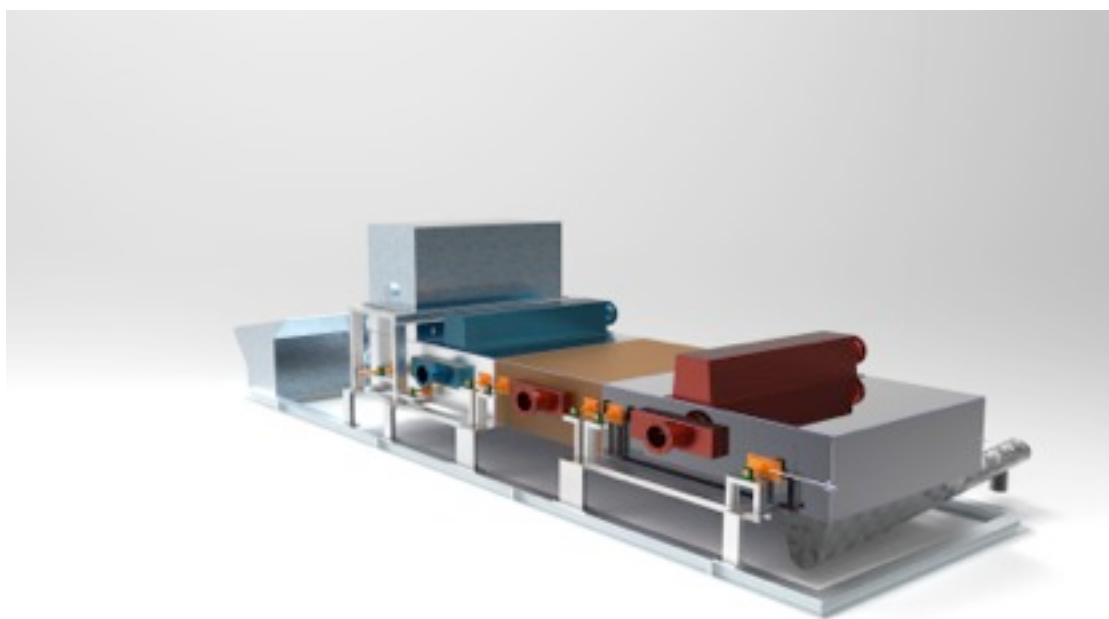
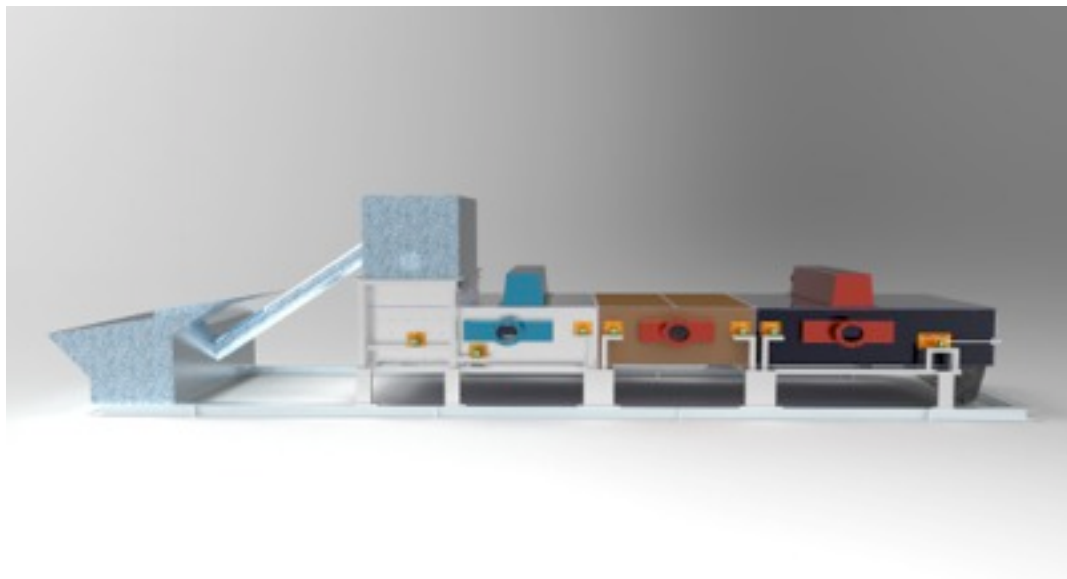
Drying temperature is best between 110 to 130 degrees Celsius. As a heat transfer media, gas from the motor exhaust is heated/regulated to the drying temperature of 110 to 130 degrees Celsius and is blown into the drying stage of the kiln. The charring kiln has a steam/gas extraction port on top where the steam laden drying gas is extracted.

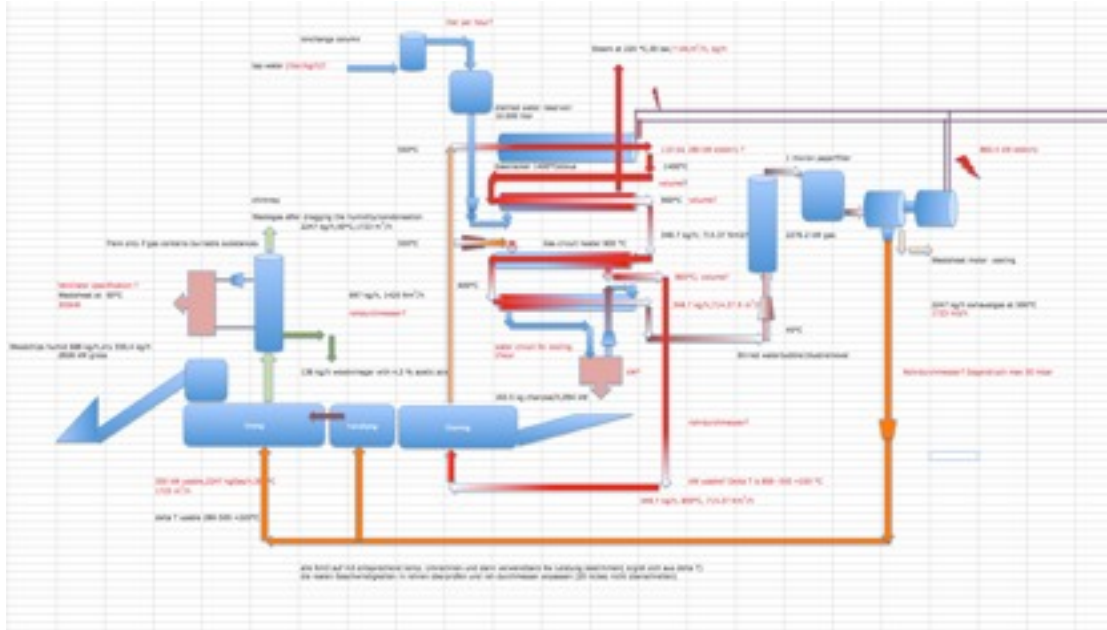
The hot gas injection ports on the side of the belt are below the belt, and the hot gas passes through belt and material layer. This avoids drying gas flowing towards the intake, and with a ventilator in the back of the condenser, sufficient vacuum is generated to avoid back filtration of gas/steam into the kiln.

In a closed loop kiln, the staged process includes a separate loop just for drying, using low temperature melting salts, thermo oils or metals as heat transfer medium to drive off humidity .

Staged pyrolysis with recovery of byproducts

The interior of the kiln is divided in several sectors where the belt moves through.





After the drying section in the second sector the heat pipe transferred or direct injected heat to char the particles is adjusted to a temperature level of 350 degrees Celsius, meaning that every particle will be heated to the core in 30 to 40 minutes, from 130 degrees Celsius to 280 - 350 degrees Celsius. The residence time in this temperature range and sector is sufficient to produce adequate out-gassing.

The gases evolving from the heated particles are in part recycled over heat exchange areas to maintain the heat transfer. (Gas inlet temperature about 500 C °, gas outlet temperature about 380 C °) The major portion of the evolving gases is sucked through a condenser to extract the valuable substances. The remaining non-condensable gases are transported towards a pulsejet or pressure burner. In case only wood chips or sawdust are charred, the drying and initial out-gassing step can be joined into one step so the condensed liquid would mainly be 80 to 85 % water and 4 to 5 % acetic acid with portions of low temperature phenols, enzymes, furans, furfural, carbonyl- and carboxylic groups as well some methanol and acetone, (wood-vinegar). This liquid usually contains, in addition to its main constituents, up to 200 different organic-chemicals, which all have effect on soil life and growth of plants.

In the third sector the particles are heated further to a temperature range between 350 to 450 degrees Celsius. In this sector, part of the evolving gases is recycled to maintain heat transfer to the material on the belt. The main portion of the evolving gases is passed directly into the gas feed line to the gas cracker.

Here the average residence time depending on raw material type is between 30 minutes to 50 minutes.

In conclusion, the configuration of the pyrolyzer itself is very flexible. In addition to the basic feeding/dosing section and the charring / dispatch section, there are optionally as many subsections as needed for extraction, drying and activation.

The throughput capacity of the device is flexible as well. By adding additional middle sections and increasing the transport rate, we can step-wise increase capacity.

From a technical / technological standpoint of view the pyrolizer has the function to transfer biologic material (mainly mixture of lignin, cellulose, hemicellulose) into char or torrefied material and/or syngas.

From an economic standpoint, the most important products to ensure financial success are not the crude char, syngas or electricity. It is the byproducts like wood- vinegar, heat at different temperatures, extracts like essential oils, aromatics, terpenes, etc, and improved or upgraded char that have the potential to generate the most income.

The char particles are deposited at the outlet into an extraction screw. The condensed and cleaned water from the drying-condensation section is sprayed onto the char inside the extraction screw, lowering the char temperature to below auto-ignition levels before leaving the kiln. The same water can be used during quenching for extraction of humics from the still hot char.

In case the material to be charred offers different temperature dependent substances, the process can be further staged at different temperature plateaus with different out gassing times to fractionate the sub-products already at the out-gassing stage.

In case of liquid heat transfer media (Liquid tin-bismuth eutectic mixture) after every decanter (hot char metal decanter) the material without contact to the outer atmosphere would enter loops at a different temperature level under atmospheric pressure or under forced vacuum to generate and separate the temperature and time dependent substances from the raw material under processing.

Management and use of the liberated heat and energy in the process

The main portion of gases from the charring section that are not used for further upgrading or processing (about 70% of the total gases produced by the pyrolyzer) are guided directly over a gas cracker, (using thermal cracking to avoid high costs for rare metal catalysts) heat exchangers and a gas cleaner into a gas turbine – motor-generator set to produce electricity. Part of that electricity is used for the kiln and the rest is sold to the grid.

As the gas cracker and gas motor or gas turbine are the main heat generators in the process, an intelligent management of this heat at their different temperature

levels allows for heat withdraw to maintain pyrolysis, upgrade withdrawn gases, or aid the in the production of byproducts.

Further processing and purification of the byproducts

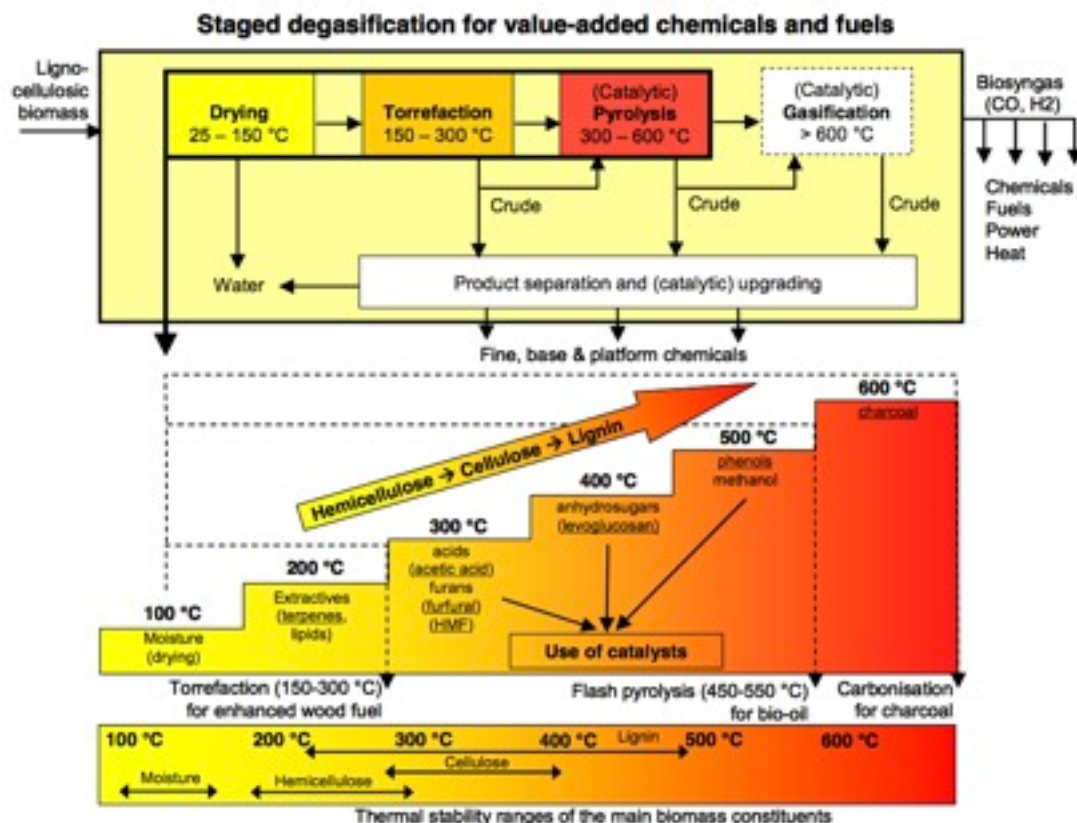
In the condenser, where gases in the temperature range of 300° to 400° Celsius are re-condensed, the following substances can be recovered, according to Wild et. al (2011):

The staged degasification concept

The fact that different biomass constituents react differently at different temperatures to yield different spectra of products can be exploited to extract value-added chemicals from biomass as a renewable route to products that can be regarded as petrochemical substitution options.

The concept of staged degasification is a low-temperature thermo-chemical conversion route to generate value-added chemicals from lingo-cellulosic biomass. Figure below presents a schematic overview of the staged degasification concept and its place in a thermo-chemical biochar process. (Taken from Paul de Wild et.al. (2011) and reduced to the concept proposed here).

By enhancing residence time at every temperature step, the charring of lignin can be concluded at lower temperatures, and the degassing of different substances shifted towards lower temperatures.



The main biomass constituents, hemi-cellulose, cellulose and lignin can be selectively devolatilised into value-added chemicals. This thermal breakdown is guided by the order of thermo-chemical stability of the biomass constituents that ranges from hemi-cellulose (fast degassing / decomposition from 200–300°C) as the least stable polymer to the more stable cellulose (fast degassing / decomposition from 300–400°C).

Lignin exhibits an intermediate-thermal degradation behavior (gradual degassing / decomposition from 250–500°C). Results obtained for beech wood in principle acknowledge the view that the chemical wood components are decomposed in the order of hemi-cellulose – cellulose – lignin, with a restricted decomposition of lignin at relatively low temperatures. In the further course of heating, a re-condensation of the lignin takes place, whereby thermally largely stable macromolecules develop.

Whereas both hemi-cellulose and cellulose exhibit a relatively high devolatilisation rate over a relatively narrow temperature range, thermal degradation of lignin is a slow-rate process that commences at a lower temperature when compared to cellulose.

Since the thermal stabilities of the main biomass constituents largely overlap and the thermal treatment is not specific, a careful selection of temperatures, heating rates and gas and solid residence times is required to make a discrete degasification possible when applying a step-wise increase in temperature.

To enhance the selectivity towards wanted products, catalysts can be applied as impregnates of the biomass, or as an external aid, e.g. in the form of injected catalyst entrained steam or gas into the charring rollers or in the form of a reactive gas (steam, hydrogen, oxygen, CO₂). Downstream treatment of the primary product vapors in a fixed bed of catalyst is another possibility.

Depending on these process conditions and parameters like biomass composition, and the presence of catalytically active materials, the product mixture is expected to contain more or less degradation fragments from hemi-cellulose, cellulose or lignin.

The staged degasification approach stands in contrast with fast pyrolysis technology, in which the biomass is rapidly (>1000°C/sec) heated up to temperatures around 500°C, causing – within seconds – a release of a myriad of thermal degradation products that are quickly (typically within 1 – 2 sec) quenched to a so-called ‘pyrolysis-oil’.

It is obvious that the extraction of value-added chemicals from this complex mixture of thermal degradation products is a challenge. In their critical review on pyrolysis-oil, Mohan et al. presents an extensive overview of pyrolysis-oil and related issues.

Whereas fast pyrolysis of biomass primarily has been developed to maximize liquid product yield, staged degasification aims at the gentle devolatilisation of thermal degradation products from the biomass.

Hence it is assumed matching the process conditions of the degasification process with the thermal stability of the main biomass constituents can influence yield and selectivity of the liberated products.

Due to the relatively mild conditions, the overall product spectrum might be less complex, more stable and less prone to unwanted secondary reactions when compared to the harsher fast pyrolysis process where all three biomass components are degraded simultaneously and at the same temperature.

Value-added chemicals from the staged degasification of biomass

Recently, a limited number of value-added chemicals from biomass have been identified in an extensive study by NREL / PNNL. From the carbohydrate fraction of the biomass (hemicelluloses and cellulose) furfural and levoglucosan are interesting value-added chemicals that can possibly be produced by direct thermo-chemical conversion.

Although several ('dry') thermo chemical processes for furfural production have been explored in the last decades, modern commercial processes to produce furfural involve mostly aqueous-phase hydrolysis / dehydration processes operating at relatively low temperatures (around 200°C) and often using catalysts like sulphuric acid.

This leaves the an-hydro sugar levoglucosan (dehydrated glucose) as the most interesting candidate that could be directly produced from the carbohydrate fraction of biomass by (staged) degasification or pyrolysis. Alternatively, staged degasification could be targeted at the production of groups of chemicals that can be upgraded using existing (petro) chemical technology like selective hydrogenation.

Examples of these groups are carboxylic acids (formic, acetic, propionic), furans (furfural, furfuryl-alcohol, furanone, hydroxy-methyl-furfural), C2, C3 and C4 oxygenates (hydroxyacetaldehyde, glyoxal, acetol), an-hydro sugars (predominantly levoglucosan) and hydroxylated aromatics and aromatic aldehydes that constitute potential thermo chemical degradation products from lignin.

It is obvious that the separation and subsequent upgrading of these groups of chemicals is easier and cheaper than the isolation of a single chemical from the complex mixture of thermal degradation products.

(From Paulus Johannes De Wild: BIOMASS PYROLYSIS FOR CHEMICALS
ISBN: 978-90-367-4993-0)

If only agriculturally usable substances are the goal, the following pathways are relevant:

The original concept from Paul de Wilds work can be adapted to a char optimized version where only the condensable substances from the drying and the condensable substances from the first pyrolytic treatment up to 350 degrees Celsius are recovered.

As biochar is the main product, and only agronomical valued substances are the secondary product, a recovery of other industrially important substances is neglected and preferably transferred to the 'heat to electricity' or "oxidation to humics" part of the charring unit.

In the first step of recovery, mainly water and some low boiling terpenes are recovered.

In the second step, terpenes, lipids, carboxylic groups (organic acids like acetic acid, maleic acid etc). Furans, furfural, HMF, an-hydro-sugars (levoglucosan) and some phenols are recovered.

Of utmost importance is to check the substances recovered by condensation for their influence in growth and plant development. Research in this area is urgent. Once the importance and function of every substance is defined, the charring process can further be developed to optimize the production of important and relevant byproducts.

Transformation of bio char into agronomical useful and applicable substrate adding fertilizer, micronutrients ad trace elements

As macronutrient addition would be too bulky, the milled char should be soaked only with micronutrients and trace elements. A water-soluble concentrate is mixed with the recovered water from the drying section, using part of the acetic acid / organics from the second condenser, and applied to the dry char until saturation of the char occurs. (ph control of the end product)

This raw material now can be mixed with clay, compost or other growth enhancing substrates and packed for sale.

Additional processes to enhance value of char and to get enhanced economic payback for the heat generated.

Fuel from Waste plastics

Heat in the range of 450 degrees Celsius (cooling of the gas leaving the cracker) can be used in a separate reactor to melt and vaporize waste plastics, passing the vapors over a set of catalyst like Y-Zeolite (perlkatalyst), ZMS 5 and other zeolytic catalyst to crack paraffins and produce a mix of diesel, kerosene and gasoline, which afterwards, using the same heat, can be fractionated in a

fractionation column. This would generate an upgraded value for the heat of a factor 20 or more.

Production of growth enhancing oxidized humics from char (Artificial wood-vinegar)

Char can be biologically oxidized by percolating water, mixed with iron sulfate, micronutrients and some acetic acid and maleic acid as well citric acid and other organic/ inorganic acids through the finely milled char.





As a source of bacteria and fungal spores liquid cow dung, waste water from pigs or chicken and some compost tee is added too.

After percolation with injected air during several days the forming bio film with bacteria is oxidizing the aromatics into aliphatics with carboxyl groups, carbonyl groups, some phenols and other oxidation products. The biologically oxidized char is then cooked with 1 molar KOH to extract all the aliphatics including the dissolving bio film. After up-concentration and sedimentation of those humic substances the process of biologic oxidation can start over again.

This is repeated until all the char particles are transformed into humics and other partially oxidized sub-products.

These substances then can be used as growth enhancing foliar sprays with dilution rates between 1 :25 to 1 :50.

Economics are main driver of process parameters and type of process

Basically the local or regional consumer price and sellable quantity of the different products defines the type of charring and byproduct production.

Just as an example char-wood vinegar-cleaned gas for electricity under different economic conditions:

In Central America one would have at the moment limited market for char, heat and wood vinegar but an excellent market for electricity. So the charring equipment would eventually focus on char efficiency around 20 % and wood vinegar around 10% but high burnable gas quantity to produce electricity.

In Europe, char, heat and wood vinegar would be priority and electricity only to substitute grid electricity but no grid feeding of electricity.

This leads to different char processes and different pre-preparation of raw material. To increase for example the char quantity from 30 to up to 42% one would impregnate raw woodchips with phosphoric acid.

To increase gas production the process would be at a higher temperature level and possibly adding of dolomite to the raw material would increase gas production and reduce char production etc.

Pyrolizer as an energy central/hub with sub products

- Sales business model 4 ton char per 24 h

In this model, the unit is built and sold to the public. This business approach will have a greater chance of success if the company leads the way in creating successful business models for its clients, rather than fulfilling the clients' request for a custom-designed pyrolysis device. In other words, we should sell a successful business model, like a franchise, to our clients, rather than just a pyrolysis device. Like a franchise model, the agreement would be structured so

that a percentage of the client's income would be paid to the parent company. In this case, the initial selling price could be lowered, but the overall income, over a number of years, significantly raised. The advantage of the franchise model would be that the parent company would not need to provide financing or assume any liability for operation, but by providing a solid business model, and the technology needed to implement it to the client, the parent company has a relatively solid assurance of ongoing income from the project.

- **Investor owned business model**

In this model, the unit is owned by an investor group and is pre-financed and maintained by the investor company. The client/operator is allowed to buy the heat and electricity at a significant discount from market rates. The contract duration is 20 years minimum, after which the ownership of the whole unit is passed on to the client without costs.

The investors receive income from the electricity and heat sold to the client/operators, as well as from the wood vinegar, extracts and char. All together these should give a payback time of 6 to 7 month, whereas revenue from the sales over the 20 year contract period would provide an investment: recovery ratio of 1: 15 or higher.

- **Hybrid investor/client owned business model**

The investor group forms an energy sales company and sub-product sales company and an engineering company.

In short time there would be 50 or more units all over the country. The sales unit can create a fertilizer company where the wood vinegar and the char are transformed into specific high value products for farming, fruit production and gardening. This company would have to process the wood vinegar from 50 or more units and the char from 50 or more units. Hence, the engineering company has a more complex set of tasks to fulfill.

The engineering company would have to develop tailor-made small hardware packages for different types of production that can produce with up to 600 kW electricity and 1 megawatt heat in different levels as dry or wet or pressurized heat (steam). (up to 10 small companies with 60 kW electric needs and 100 kW thermal needs could be located as satellites around the hub)

These units would be targeted to small scale industries in the area such as bakeries; laundry; spice drying and fermentation; essential oil extraction; oil extraction; water or water alcohol extracts with freeze drying to up-concentrate and stabilize the high value extracts; steam cleaning for cars and motors; high pressure steam explosion to prepare raw material for high efficiency extraction or biogas fermentation or paper making; emergency kitchens in catastrophe situations which need lots of heat for sterilization; cooking, cleaning, disinfection; heat for heating and warm water and electricity as well air-conditioning for small hostels or hotels or bungalows; small Ceramics workshop etc..

These are simply a few initial ideas. There are endless small satellite packages possible which are based on selling energy in different levels with flexible coproduction of char and wood vinegar. Manufacturing plants that have a need for process heat or steam could also be targeted.

This model requires that the investor company retains ownership of the hardware for the first 20 years for the small-scale satellite production units or industries.

Only after the hardware is fully financed/ paid back with interest through the operation, and the business has proven that the trained entrepreneurs are capable to run this satellite industry alone, free of debt and economically viable with a solid marketing and sales infrastructure, then the investor group can transfer the ownership of the hardware to those entrepreneurs while still participating as a minor share holder in the small business. This would provide an incentive for these businesses to both join and remain with our program, as they would be working toward full ownership of the plant.

As all parts, pyrolizer and satellite industries are easy to dismantle and to set up at a different location; flexibility is provided in a wide range.

Accompanying the entrepreneurs in perfecting their skills (specialized training in running the machinery, product quality control, book keeping, marketing and sales training), gives the investor the security that he has hundred percent control over his investment, so his income forecasts are secure and correct.

Having the energy infrastructure and the hardware financing solved and stretched over 20 years gives the entrepreneur the possibility to focus on production, marketing and sales. Since the investor remains in the background, out of own financial interest, with financial and logistic backing, this relationship strengthens the business and secures income for both parties.

The raw material provider will likely be in the wood industry, forestry or large scale farming because these industries have huge waste streams that impose costs and are potentially an environmental pollution factor. Since the business systems would provide a source of revenue for such firms, they are natural partners to the investor group, selling their processing waste or production/ harvest waste at a reasonable price. This extra income could provide investment capital for the pyrolizer and satellite industry model.

As the whole chain is split into hundreds of small industries, the danger that market changes or management incapacity brings the whole business to a point of failure is negligible, particularly in that there will always be a need for energy.

As most of those activities have a high social and self-employment factor, the taxes and subsidies should be more favorable for the investors as well.

The business model is an excellent mix of control of the whole financing chain on one side and entrepreneur freedom of daily decisions on the other hand.

Building a business, training specialized and higher skills and earning money in the whole chain is the best way to strengthen a civil society, to create jobs and income for all. As this process of creating new streams in the economic environment is in private hands, poor economic decisions are much less probable than would be the case with, for instance, government-run programs to foster business and employment, which have proven to be both ineffective and have high corruption and mismanagement potential.