# PRODUCTION OF AGRI-CHAR AND ENERGY FROM RECYCLED ORGANICS

***"WMMA BREAKFAST MEETING-JUNE 2005"***

BEST

# BEST TECHNICAL PROFILE

**Clean Air**
- De NOx Box
- Scrubbers
- Filters
- Cyclones

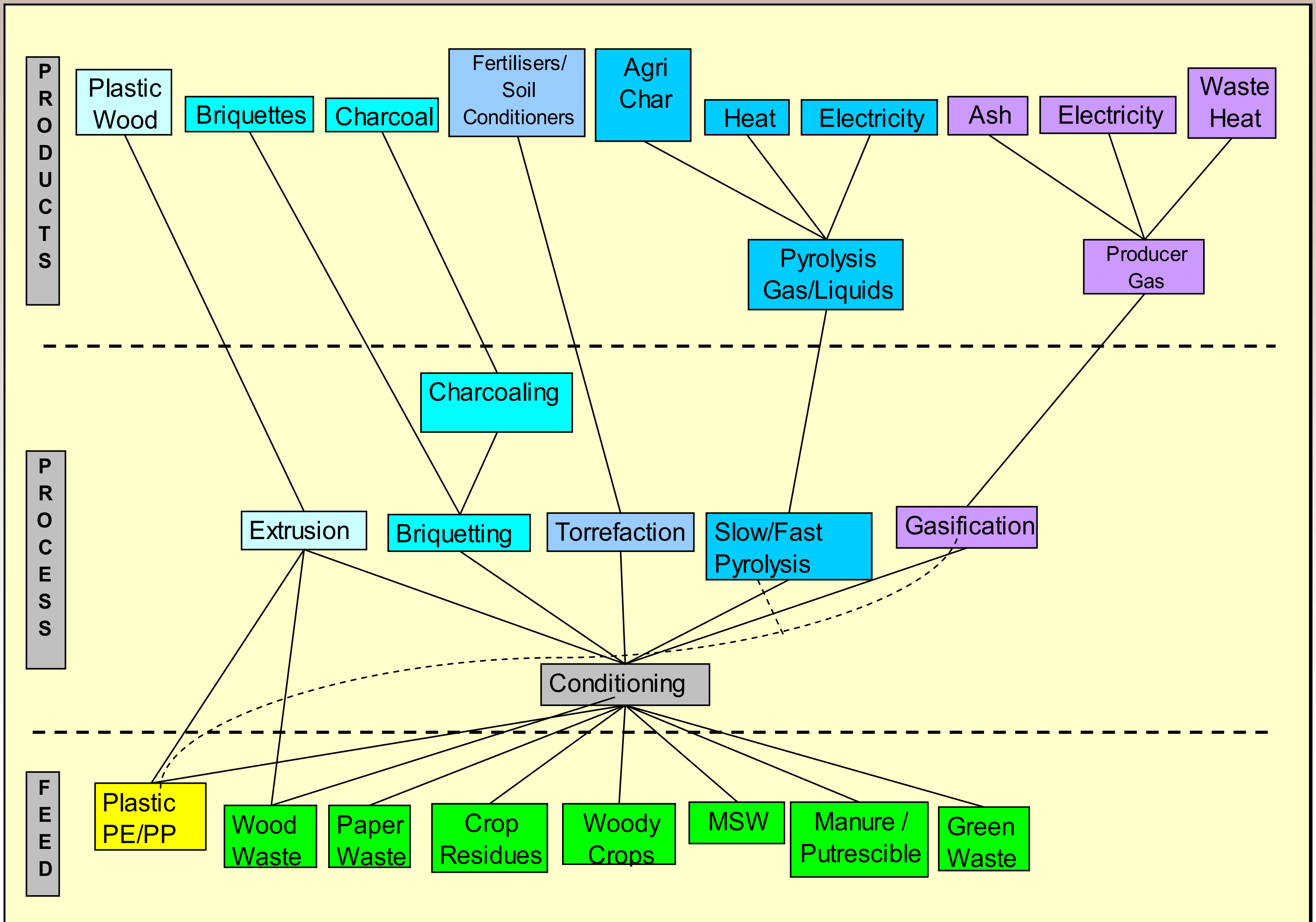
**Clean Combustion**
- Flares
- Reburners
- Gas Turbine Combustors
- Porous Burners

**Clean Fuels**
- Briquettes
- Charcoal
- Liquid Biofuels
- Algae

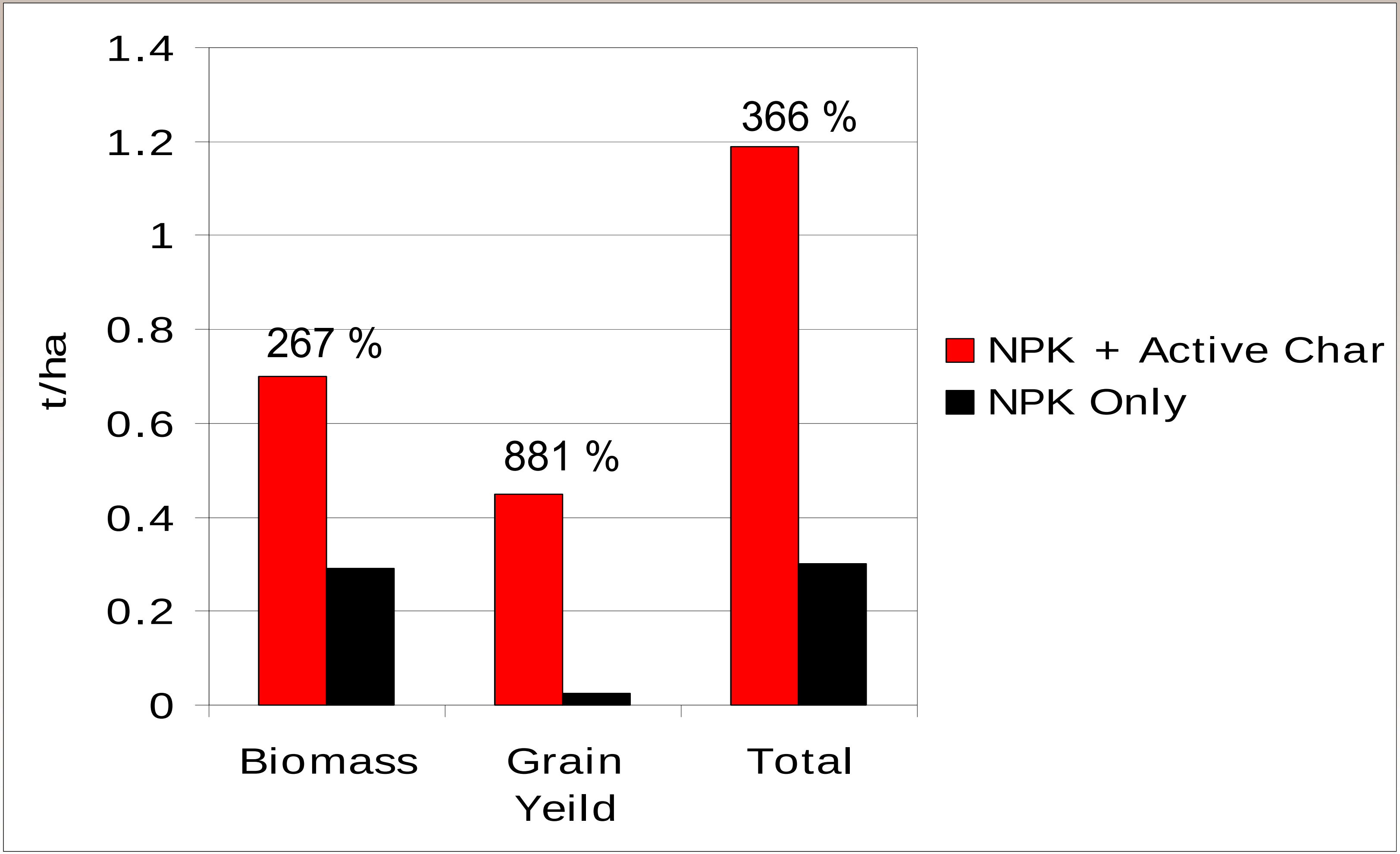
**Clean Energy**
- Pyrolysers
- Gasifiers
- Fluid bed CHP
- Biogas Plant

**Recycled Products**
- Agri-char
- Plastic Wood
- High Silica Ash
- Bio-fertilisers
- Compost

# PATHWAYS FROM WASTE TO PRODUCTS



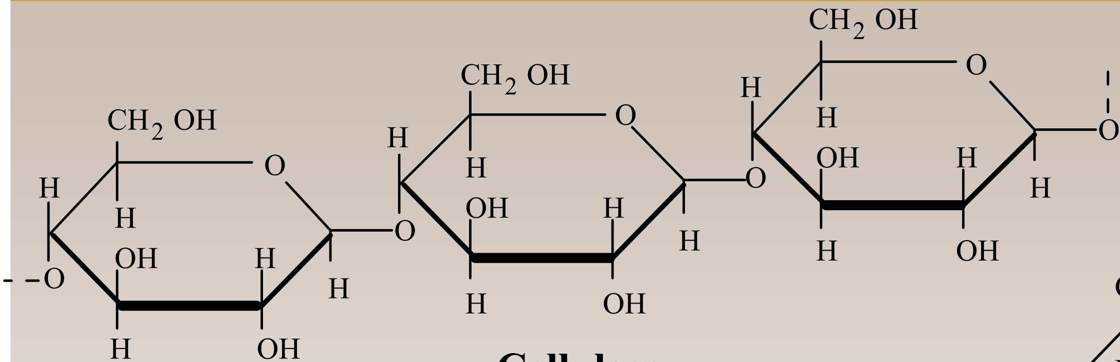
# Influence of char on crop growth: Sorghum @ 55 days




Steiner, C. et al (2003), University of Bayreuth, Germany. “Slash and char not slash and burn”

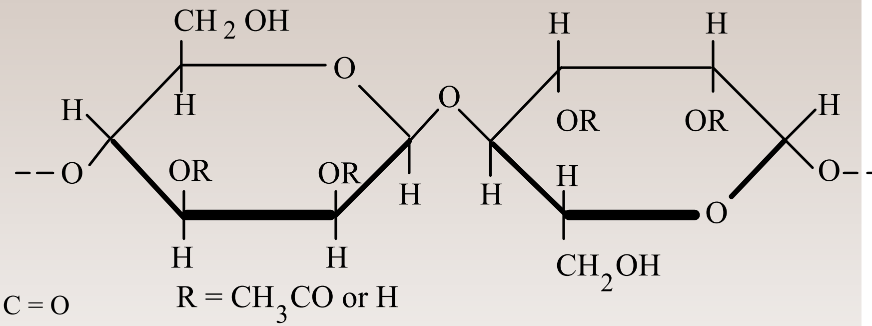
# Migration of Char to Plant Roots, Increase in Microbial and Entomological Activity and Improvement in Pest Resistance

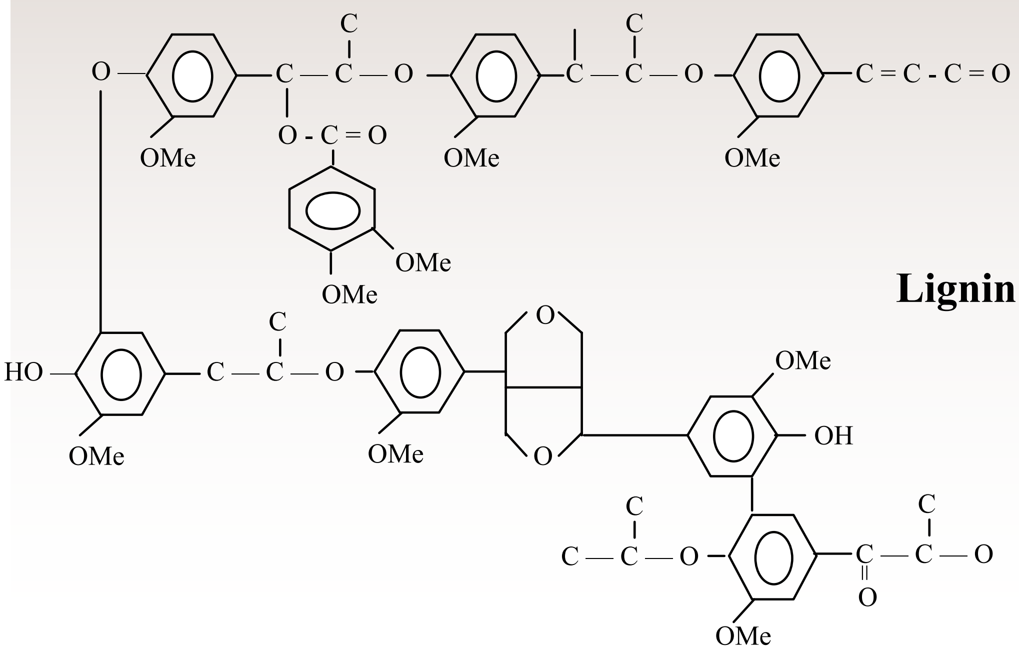
# The Chemical Structure and Nature of Biomass



**Cellulose**

**Softwood Hemicellulose**





**Lignin**

Cellulose and Hemicelluloses are polysaccharides. Lignin is composed of phenolic polymers composed of C3-C6 phenyl propane units. Lignin is the amorphous material that surrounds cellulose fibres in the middle lamella and cements them together. Lignin is a random, three dimensional polymer made up of phenyl propane units where the unit may either be a guaiacyl, syringyl or hydroxyl.

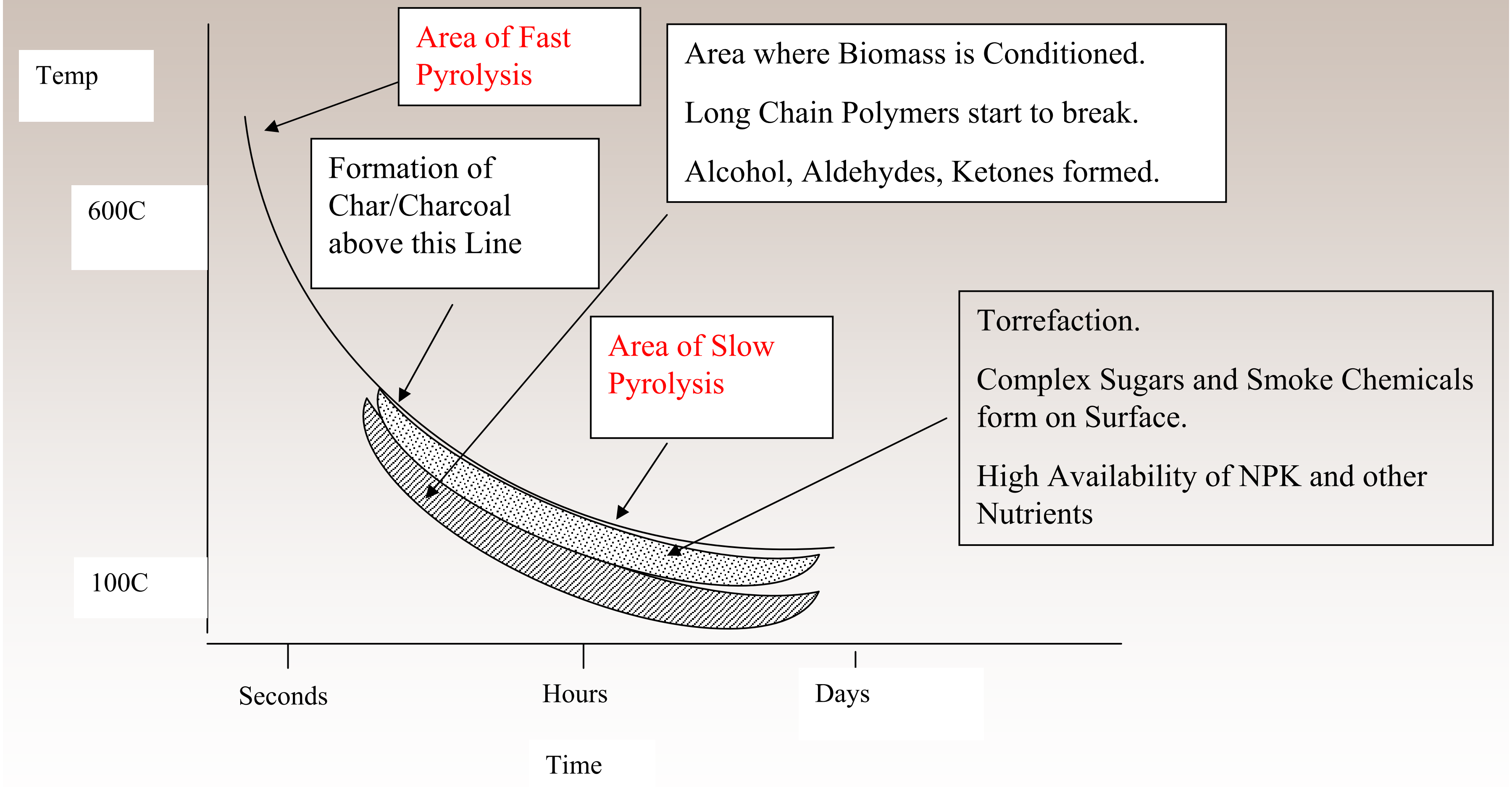
# Typical reported analyses of different biomass [wt% dry ash free]

| Biomass | Ash | Extractives Solvent Soluble | Extractives Water Soluble | Lignin | Hemic | Cellulose |
|---|---|---|---|---|---|---|
| Hardwood | 0.3 | 3.1 | -- | 19.5 | 35.0 | 39.0 |
| Softwood | 0.4 | 2.0 | -- | 27.8 | 24.0 | 41.0 |
| Bagasse | 1.6 | 0.3 | -- | 20.2 | 38.5 | 38.1 |
| Rice straw | 16.1 | 4.6 | 13.3 | 11.9 | 24.5 | 30.2 |
| Wheat straw | 6.6 | 3.7 | 7.4 | 16.7 | 28.2 | 39.9 |

# THERMAL TREATMENTS USED TO PRODUCE STERILE SOIL ENHANCERS AND FERTILISERS FROM ORGANICS

- **AUTOCLAVING FOLLOWED BY DRYING AND PELLETISING TO PRODUCE STERILE PRODUCT THAT IS EASIER TO BREAK DOWN BIOLOGICALLY.**
- **AUTOCLAVING AND BIOREACTION FOLLOWED BY DRYING AND PELLETISING (BIOFERTILISERS).**
- **HIGH TEMPERATURE STEAM HEATING AND THEN PELLETISING UP TO 180C (CONDITIONING).**
- **HEATING IN ABSENCE OF AIR TO 180-250/300C (TORREFACTION) TO BRING OUT SUGARS AND STARCHES, SMOKE CHEMICALS FOR GERMINATION. BIOMASS STERILISED.**
- **HEATING IN ABSENCE OF AIR BETWEEN 300 AND 600C TO PRODUCE CHAR (PYROLYSIS), BIO-OILS AND SYNGAS. FIXES MINERALS AND CARBON. CAN PRODUCE CHEMICALS THAT INHIBIT PLANT GROWTH.**
- **HEATING IN ABSENCE OF AIR TO 500-650C AND THEN INJECT VERY HOT AIR AND STEAM TO PRODUCE ACTIVE CHAR. HIGH POROSITY; NO CHEMICALS THAT INHIBIT PLANT GROWTH.**

# Summary of Reaction Kinetics and Products for Thermal Decomposition of Biomass



# Chemical Changes in Conditioning and Torrefaction

- The Degree of Polymerisation Decreases from 10,000 to 500 as the material is Heated to 200C. The Polymers Become Highly Active.
- Chemical Water and $CO_2$ Released As Polymers Break Down. Weight Loss (on oven dry basis) about 20% at 250C
- Surfaces become Dark Yellow Brown with breakdown products of the lignin
- Complex Sugars Formed on the Surface of the Biomass
- Humic and Fulvic Acids Plus other Complex Compounds in Small Quantities on the Surface of the Material.
- Electrical Conductivity is still High and most Minerals are Available to Plants through Dissolution and Microbial Action
- Below 250 C Hydrophilic Carboxylic Acids (Formic and Acetic, Methanol), Anhydroglucoses and Furanoic Compounds. Levoglucosan is the Dominant Carbohydrate. The Condensable Lipophilic Compound Groups Include Fatty and Resin Acids, Fatty and Triterpenoid Alcohols.
- Pot Trials Show Good Plant Response to Torrefied Cow Waste/Saw Dust

# Chemical Changes in Pyrolysis from 250 to 450C

- The Volatile Gases Coming from the Decomposition of the Biomass React with the Polymers to Produce a Non Crystalline Aromatic Type Structure
- Two Reaction Mechanisms have been Proposed

  1. Macropolymers → Active (1) → Bio-Oils (3)→ Gas (Fast Pyrolysis)

  2. Macropolymers → Active (1)→ Char + Gas/Bio-Oils (Slow Pyrolysis)
- The Reactions Are Exothermic.
- The Rate of Reaction Depends on the type and Amount of the Metals In the Char
- Most of the Bio-Oils are Larger Molecular Weight compounds ($C_xH_yO_z$).
- Bio-oils Fill Most of the Pores and Cracks Between the Amorphous Carbon
- Electrical Conductivity is still High and most Minerals are Available to Plants through Dissolution and Microbial Action
- Yields of Char vary from 30% to 60%.
- Work in US Show Mixed Results in the Effect on Germination Rates and Plant Growth

# Typical Chemicals in the Volatile Gases Produced During Low Temperature Pyrolysis (above 250C)

| Component Type | Typical Compound | Formula/MW |
|---|---|---|
| Syngas | Methane, Hydrogen, CO, $CO_2$, H20,$C_2H_2$, $C_2H_4$ | |
| Acids | Formic | $CH_2O_2$ |
| | Acetic | $C_2H_4O_2$ |
| | Butanoic | $C_4H_8O_2$ |
| Sugars | Xylose/Levoglucosan | $C_6H_{10}O_5$ |
| | Glucose/Fructose | $C_6H_{12}O_5$ |
| Alcohols | Methanol | $CH_4O$ |
| | Ethanol | $C_2H_6O$ |
| Ketones | Butanone | $C_4H_6O$ |
| | Cyclohexanone | $C_6H_{10}O$ |
| Aldehydes | Formaldehyde | $CH_2O$ |
| Phenols | Cresol | $C_7H_8O$ |
| Guaiacols | Guaiacol | $C_7H_8O_2$ |
| Syringols | Syringol | $C_8H_{10}O_3$ |
| Furans | Furfural | $C_5H_4O_2$ |
| Mixed Oxygenates | Resorcinol | $C_6H_6O_2$ |

# Chemical Changes in Pyrolysis from 450 to 600C

- The Volatile Gas Production is Reduced and mainly Comes from the Diffusion of Bio-oils from the Pores.
- These Volatiles Probably still React within the Residual Biomass Polymers to Produce a more Aromatic Structure.
- The Reactions Are Endothermic and there is a more loss of mass.
- The Rate of Reaction Depends on the Type and Amount of the Metals In the Char.
- More Complex Aromatic Bio-Oils are formed in the Gas Phase (Indene and Napthalenes).
- Bio-oils Start to Leave Micro and Macro Pores.
- Some of the Reactive Alkali Metals are Volatilised but much of the Nitrogen is Retained within Aromatic Compounds.
- Electrical Conductivity is still Lower and most Minerals become locked into the Char Structure Available to Plants through Dissolution and Microbial Action.
- Yields of Char vary from 30 to 60%.
- There are more Reactive Carbon Bonds at Edges/Surfaces

# Activation of Char at 550C to 650C with very Hot Air and Steam

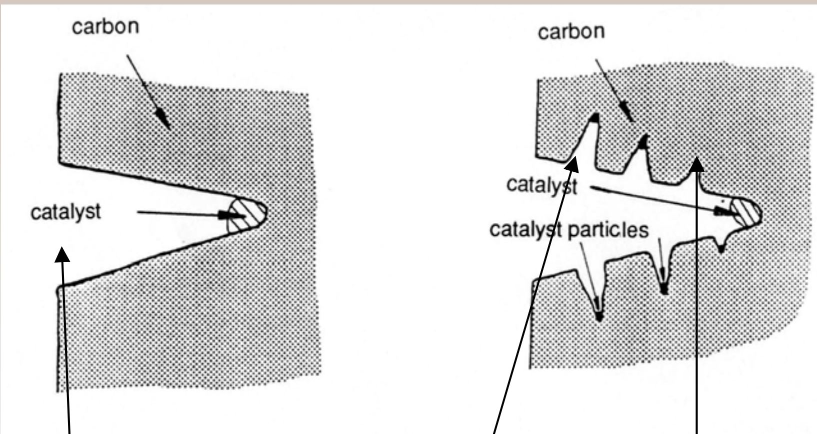
- Significant Increase in Porosity especially at 650C. Surface Area is usually higher than 400$m^2$/g and Absorption Volume is .4$cm^3$/gm.
- Some Graphite Structures are formed within the Amorphous Matrix.
- Highly Active Surface Sites with residual valencies and unpaired electrons on Carbon that can absorb Nutrients and Toxins (Very High Cation Exchange Capacity of Char).
- Metals Form Complexes (usually Oxides, Sulphates and Chlorides) and are Locked Up.
- Some Alkali Metals Volatilised
- Active char produced from chicken litter has been analysed to have a high nutrient content:
- Nitrogen 3.52%, Phosphorous 4.4%, Potassium 3.8%, Silicon 5.8%.
- Other trace minerals include Boron, Manganese, Iron, Magnesium, Copper

- Pot and Field Trials in Asia, Europe and Latin America Positive Results
- Can Add Ammonia Salts to increase Nitrogen Content Either with Feed Stock or After formation of Agri-Char

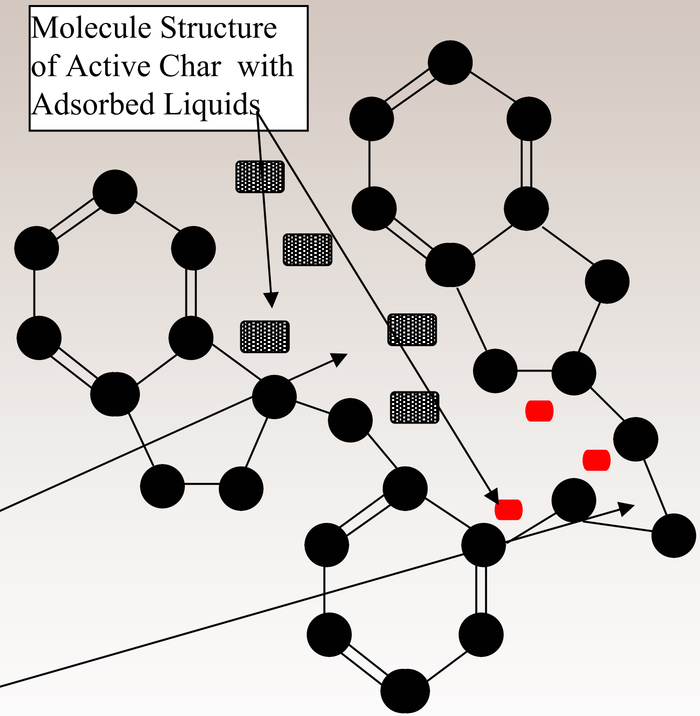
# Outline Structure of Active Char in Agri-chars

At the temperatures for Agri-char production most of the carbon is not in a graphite form. However there are pockets of ordered carbon atoms.

Metal atoms with steam and Air react with the Complex Carbons to give Pores with Active Surfaces




Figures 13 (a) and (b). Channeling action of a catalyst resulting in fluted channels




Macro-Pores >50nm

Meso Pores 2-50nm

Micro-Pores

# Outline Structure of Graphite in Active Agrichars

In graphite, there is both σ- and π- bonding holding the atoms in hexagonal two-dimensional networks. These layers are held rather loosely together by van der Waals forces. The stacking of the layers is principally – A.B.A.B., the hexagonal form, illustrated in Figure 3, with a small proportion (<10%) in natural graphite's stacked – A.B.C.A.B.C., i.e., the rhombohedral form:

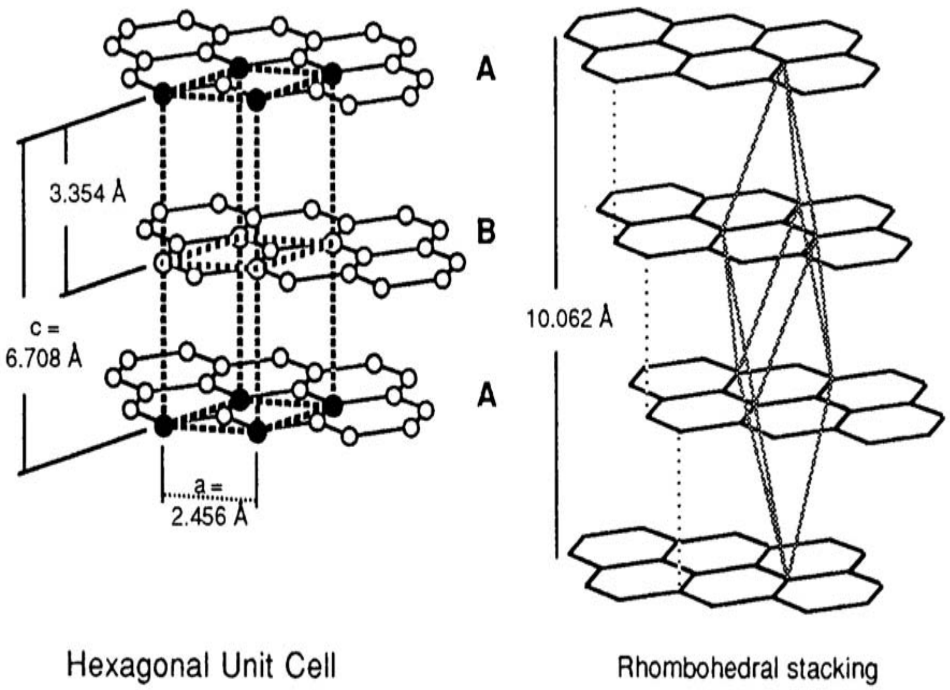



Figure 3. Graphite structure.

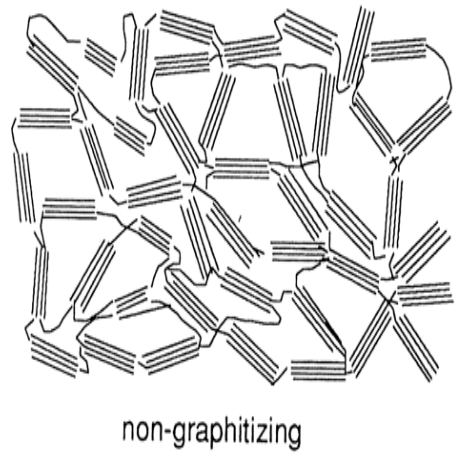
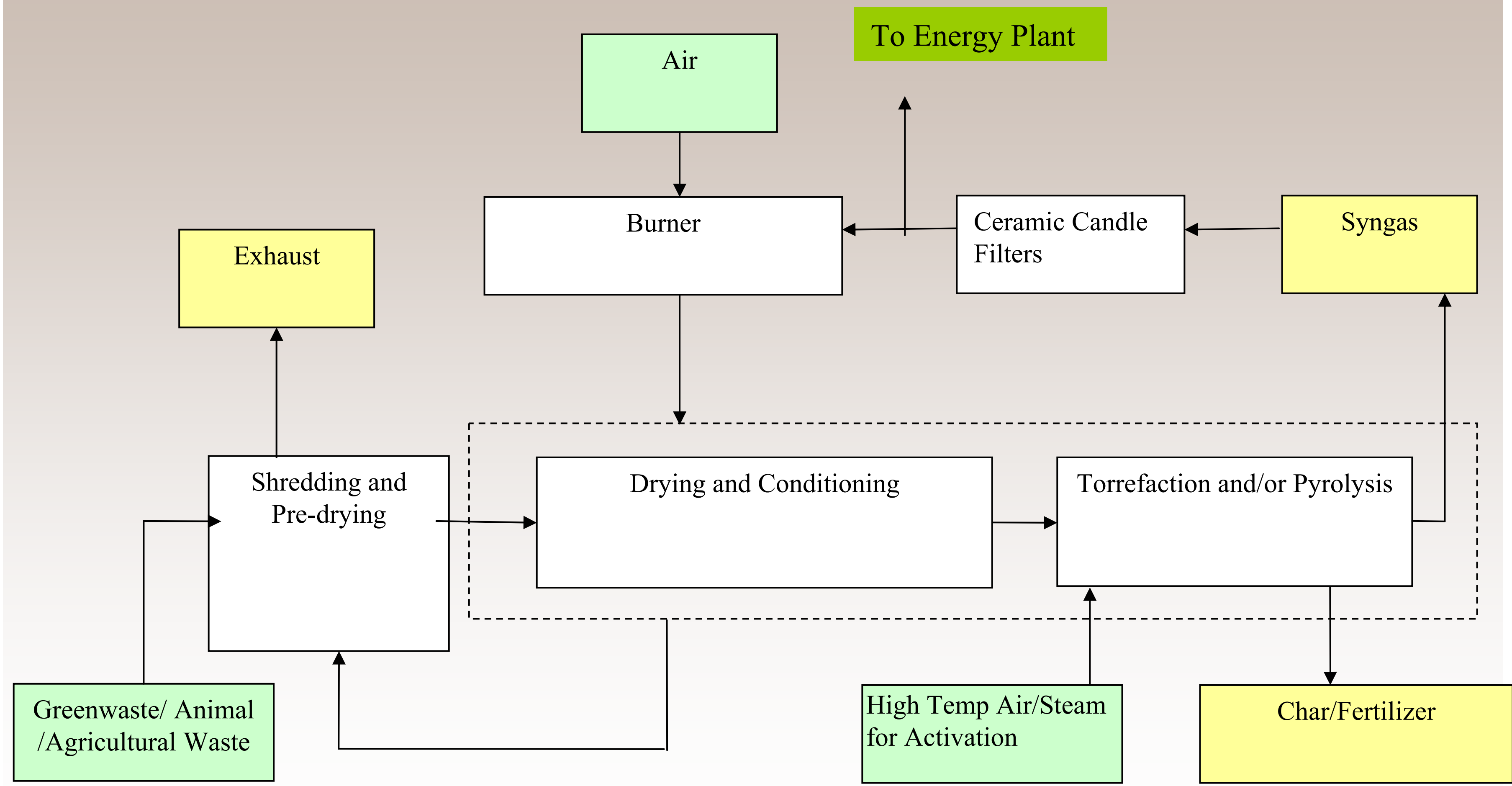



Figure 4. Franklin (1951b) models of carbon structures.

# How is Agri- Char Manufactured From Animal and Biomass Waste?

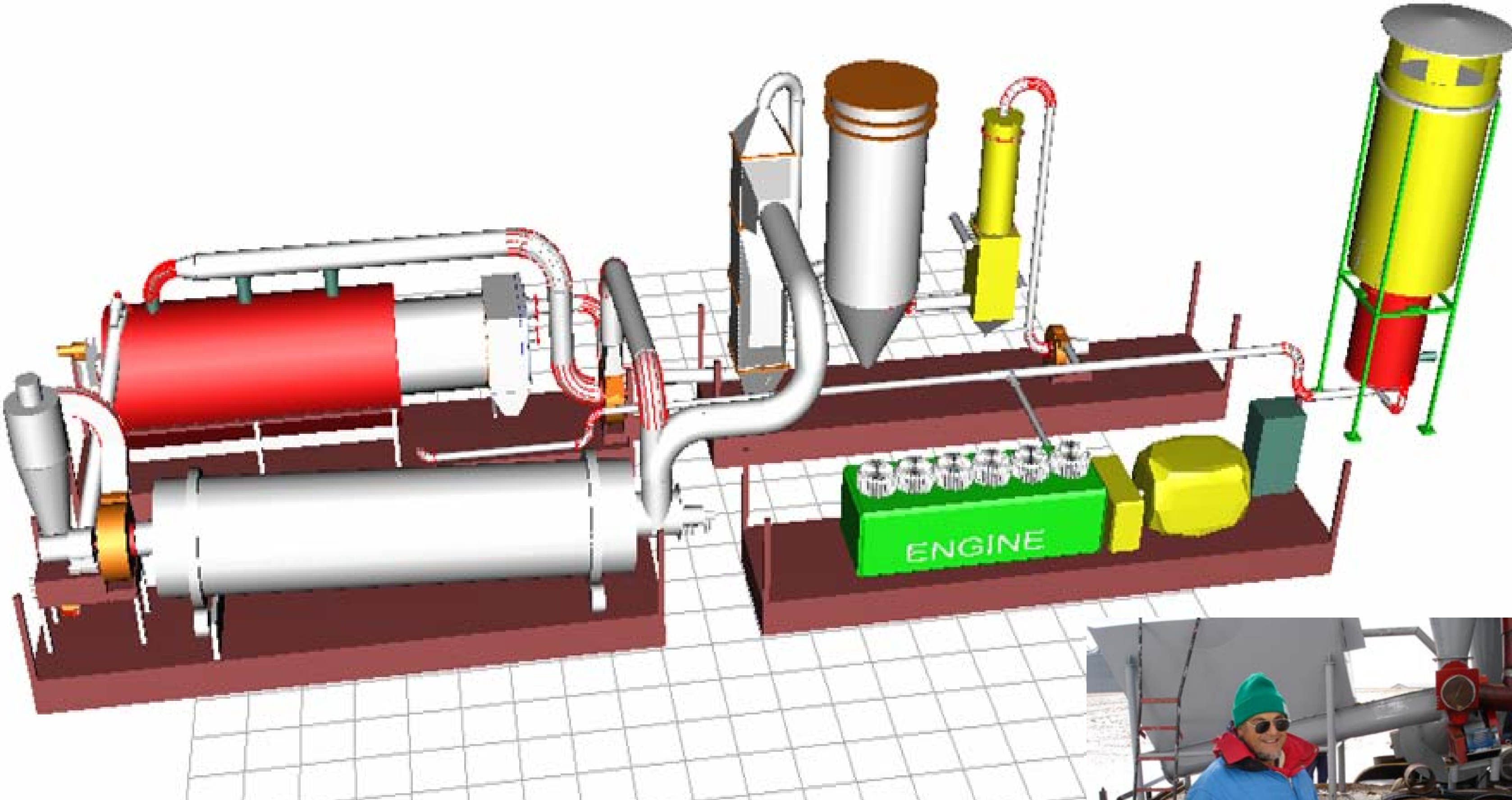


# How is Active Char Manufactured From Animal and Biomass Waste?

- Sufficient dry biomass waste is added to the animal waste to reduce the moisture content (less than 30%).
- The material is fed to the drum reactor unit and heated to between 250 and 600$^{o}$C
- Small amounts of steam/air are added at the back of the reactor when Activation is required.
- The reactor produces a medium calorific value synthesis gas used for heating the reactor drum and also for producing energy.
- Gas must be cleaned and cooled for energy production. During cooling bio-oils are produced.
- Initial starting heat is provided by LPG or NG.

# B E S T Agri-Char Unit Operating at Moree on Green Waste; Financial Assistance From DEC

# Production of Energy, Bio-Oils and Agri-Char. Design for Cashton Area Development Authority




Char From Dairy Waste at -10C. Cashton March

No it isn't Santa Claus. Just 6 Layers of Clothes

# Cashton Green Energy Park

On Site:

- Bio-Refinery to produce green energy and marketable products
- Bio-Diesel processing & fueling
- Two (2) Utility scale wind turbines
- Plans to use cow manure as feedstock for bio-refinery
- Tenants will be users of the energy created on site