ASTT CONFERENCE

Combustion characteristics of coal and biofuels and the ideal biofuel

Mike Stockbridge

INTRODUCTION

An alternative to steam coal would be briquettes (ovoids) manufactured from biomass, but with the components modified and mixed to burn with coal characteristics.

Coal briquettes used to be widely manufactured as “Loco Nuts” for steam transport use.

- Particulate coal plus a binder.
- Mixed and pressed into oval shapes.
- A common binder was coal tar from gas works.

Charcoal briquettes are currently manufactured, both in developed countries for BBQ use, and in developing countries for cooking.

Both the production of carbon biochar from biomass, and the manufacture of fuel briquettes are old and mature technologies.

The problems with currently produced charcoal BBQ briquettes are the high cost (from the BBQ market), slow burning rate and low strength (many products reportedly break-up in the firebox).

This presentation is a literature study to look at possibilities and disadvantages of using biofuels in briquette form for heritage steam applications.

INTRODUCTION

There is a huge amount of information and ongoing research into biofuels:

- 3rd world heating + cooking (Africa, India, Far East).
- Densification of biomass to reduce transport costs.
- Consolidation of coal fines (China).
- Consolidation of lignite (China).
- Densification of mineral ores.

Commercial production:

- BBQ briquettes.
- Home heating briquettes.
- 3rd world heating + cooking (Africa, India, Far East).
- Industrial applications.

Typical size/shape – Ovoids 50mm (2”) and 75mm (3”).
Typical weights: 150 gm and 75 gm.

INTRODUCTION

COMPARATIVE COSTS:

- Coal price £450 / tonne – bulk
- Barbecue market - Charcoal price £1000 - £2000 / tonne – retail
- Price for HVO (Hydrotreated Vegetable Oil) is about 10% more than fossil heating oil.

COMPARISON OF CALORIFIC VALUES

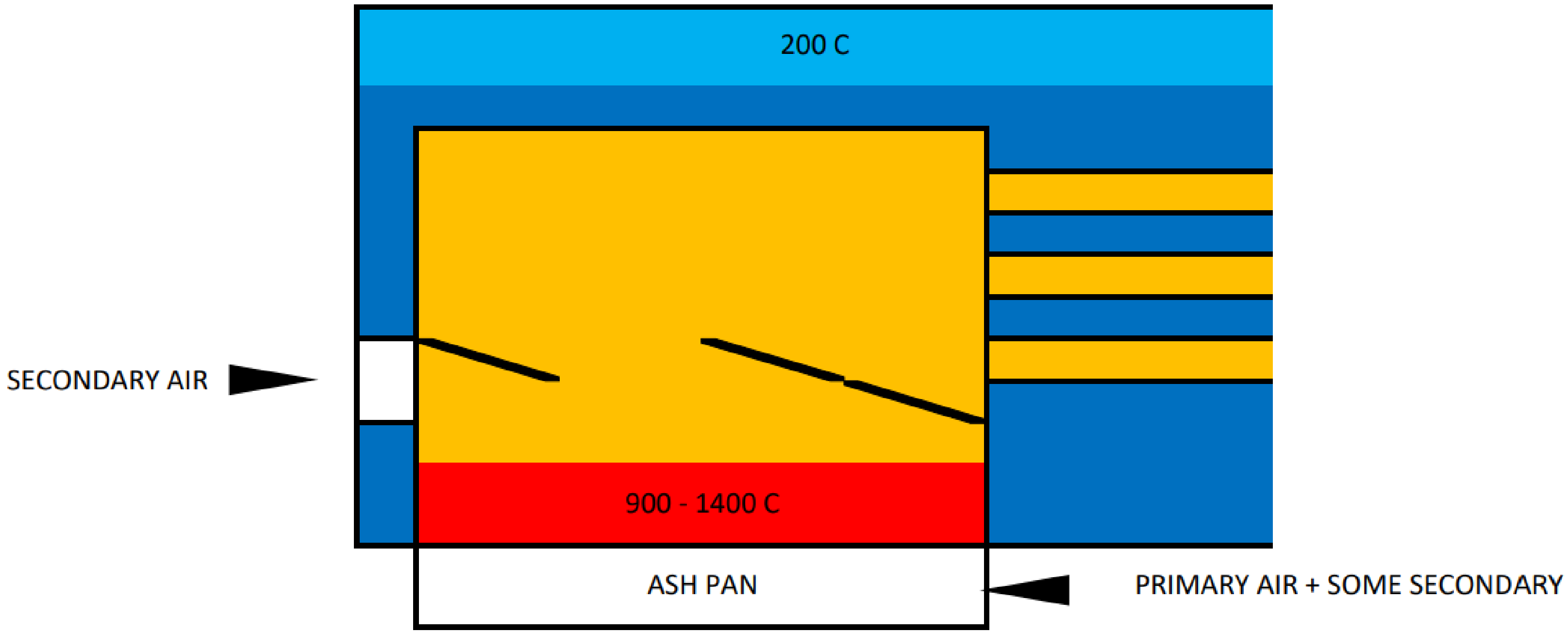
Coal (Ffos-y-Fran)
Lower Calorific Value LCV = 30 MJ/kg (about 30 GJ/m3)
Bulk density depending on; particle size, impurities, moisture - in the range of 700 to 1100 kg/m3.

Bio coal (torrified cellulose from sugar cane)
Lower Calorific Value LCV = 24 MJ/kg (16.0 GJ/m3)
Bulk density = 670 kg/m3

Wood pellets – as used in Drax power station
Lower Calorific Value LCV = 17 MJ/kg (12.7 GJ/m3)
Bulk density = 750 kg/m3

HVO heating oil
Lower Calorific Value LCV = 38 MJ/kg (33.4 GJ/m3)
Bulk density = 880 kg/m3

OVERVIEW OF COAL COMBUSTION IN A LOCOMOTIVE FIRE BOX



Primary combustion solid carbon in the firebed.

Secondary combustion of CO and VOC (Volatile Organic Compounds) in the firebox, above the firebed.

OVERVIEW OF COAL COMBUSTION IN A LOCOMOTIVE FIRE BOX

In fire bed - primary air flow

- Carbon combustion - reduction of carbon to CO – $2C + O_2 + 3.76N_2 \rightarrow 3.76N_2 + 2CO$
- Volatiles release: pyrolysis (distillation), gasification.
- Sulphur combustion - $S + O_2 + 3.76N_2 \rightarrow 3.76N_2 + SO_2$
- Moisture evaporation.
- Heating of primary air.
- Heating of charged coal.
- Release of ash to the ash pan and into the air/gas flow.

Firebed VOC (Volatile Organic Compounds) release:

- Release of volatiles similar to gas works distillation.
- Formation of coke.
- Coke is stable lattice structure in a fire and has a high surface area for carbon combustion.
- Coke stability maintains air passages through the firebed.

Important to maintain air flow through the firebed with a good void space ratio and low delta pressure loss.

- Lump coal stability and volatiles release.
- Large coke surface area after volatiles release to allow for rapid carbon combustion.
- Prevention of ash and clinker build-up.

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OVERVIEW OF COAL COMBUSTION IN A LOCOMOTIVE FIRE BOX

The temperature colour range:

Red
Just visible: 525°C
Dull: 700°C
Cherry, dull: 800°C
Cherry, full: 900°C
Cherry, clear: 1,000°C

Orange
Deep: 1,100°C
Clear: 1,200°C

White
Whitish: 1,300°C
Bright: 1,400°C
Dazzling: 1,500°C

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OVERVIEW OF COAL COMBUSTION IN A LOCOMOTIVE FIRE BOX

In firebox above firebed - secondary airflow

- CO combustion - reduction of CO to CO2 – $2CO + O_2 + 3.76N_2 \rightarrow 3.76N_2 + 2CO_2$
- Hydrogen combustion - $2H_2 + O_2 + 3.76N_2 \rightarrow 3.76N_2 + H_2O$
- Combustion of distilled gasses - pyrolysis products from coal.
- Carry over ash.
- Brick arch to extend gas combustion path length.

Regulation of secondary air by opening of the firehole door and using smoke colour as a guide.

- Secondary air entering through the firehole will have minimal preheating.
- Fire hole door deflectors.
- Radient heat from the firebed.
- Rapid gas cooling from firebox walls.
- VOC combustion time in firebox.
- Firebox volume is a factor in volatiles combustion.

Auto Ignition Temperatures:

Hydrogen	535°C
Carbon monoxide	609°C
Volatile Organic Compounds	500°C to 620°C

OVERVIEW OF COAL COMBUSTION IN A LOCOMOTIVE FIRE BOX

Total air requirement:

- Stoicometric air.
- Excess air – about 20% in locomotive firing (grey smoke) and considerably less in large power plants.
- Air = O_2 - 23%wt (21%vol) + N_2 - 77%wt (79%vol).

Locomotive firebox residence time typically less than 0.5 seconds.

- Very little time for VOC combustion.
- Loss of unburned VOC fuel.

If insufficient secondary air and/or temperature and/or residence time, smoke created and fuel is wasted.

- Unburned fuel expelled with exhaust - VOC plus solid particles.

Smoke plume - ash, unburned carbon, unburned volatiles.

- Black smoke – loss of carbon particles.
- White smoke – loss of VOC.
- Exhaust steam + H_2O gas from fuel.

OVERVIEW OF COAL COMBUSTION IN A LOCOMOTIVE FIRE BOX

Stack emissions:

- From complete combustion: - CO_2, H_2O, SO_2
- VOC from incomplete combustion.
- Nitrogen gas (heat loss) + NO_x emissions..
- Excess air.
- Moisture as H_2O gas.
- Particulate ash.

NO_x includes; nitric oxide (NO) and nitrogen dioxide (NO_2), the nitrogen oxides that are most relevant for air pollution. It does not include nitrous oxide (N_2O) a fairly inert oxide of nitrogen.

NO_x gases are usually produced from the reaction between nitrogen and oxygen during combustion of hydrocarbon fuels in air; especially at high temperatures (above ~1200°C).

Ash

- Large particles fall into the ash pan.
- Solidified molten ash (clinker) on fire bars and in ash pan.
- Ash blockage of air paths.
- Particulate ash through tubes to the smoke box.
- Birdnesting of fused ash on tubeplate.
- Small particles in smoke box.
- Micro particulate ash expelled with the exhaust.

DISTILLATION OF COAL

Data from Town Gas – Gas works - Pyrolysis of coal.

- Coal - 1 ton converts to:
- Coal gas - 4000 ft3 (113 m3).
- Coke - 15 cwt (about 75wt%).
- Ammoniacal liquour - 30 gal.
- Benzole (benzene + toluene) - 3.5 gal.
- Coal tar.
- Spent oxide (sulphur).

Coke - 100% Carbon + some ash.

Coal gas (average from several sources).

- 50% Hydrogen H2
- 32% Methane CH4
- 8% Carbon Monoxide CO
- 4% Ethylene C2H4
- 6% Nitrogen N2
- Carbon Dioxide CO2
- Hydrogen sulphide H2S

DISTILLATION OF COAL

Aqueous Ammonical Liquor - Many compounds, but primarily:

- Ammonia NH_3
- Methanol CH_3OH
- Acetic acid CH_3COOH

Coal tar

- Coal tar is a mixture of approximately 10,000 chemicals - principally benzine C_6H_6 and napthaline $C_{10}H_8$.
- Plus: toluene, xylenes, cumenes, coumarone, indene, benzofuran, acenaphthene, fluorene, phenol, cresols, pyridine, picolines, phenanthracene, carbazole, quinolines, fluoranthene.
- Many of the chemical compounds are polycyclic aromatic hydrocarbons
- 4-rings: chrysene, fluoranthene, pyrene, triphenylene, naphthacene, benzanthracene,
- 5-rings: picene, benzo[a]pyrene, benzo[e]pyrene, benzofluoranthenes, perylene,
- 6-rings: dibenzopyrenes, dibenzofluoranthenes, benzoperylenes,
- 7-rings: coronene)methylated and polymethylated derivatives, mono- and polyhydroxylated derivatives, and heterocyclic compounds.

PROPERTIES OF COAL

- Brown coal.
- Bituminous coal.
- Steam coal.
- Anthracite.

IDEAL STEAM COAL

Steam coal should burn with relatively little smoke, produce limited amounts of ash and produce maximum heat.

As it burns, steam coal should fissure to release volatiles but not crack into small pieces or swell.

The carbon content of the bituminous coal present in most of the UK coalfields is 86% to 88% (Ultimate analysis).

The carbon content of anthracite is higher than bituminous coal.

Coal can be stored in the open air.

PROPERTIES OF COAL

Proximate analysis

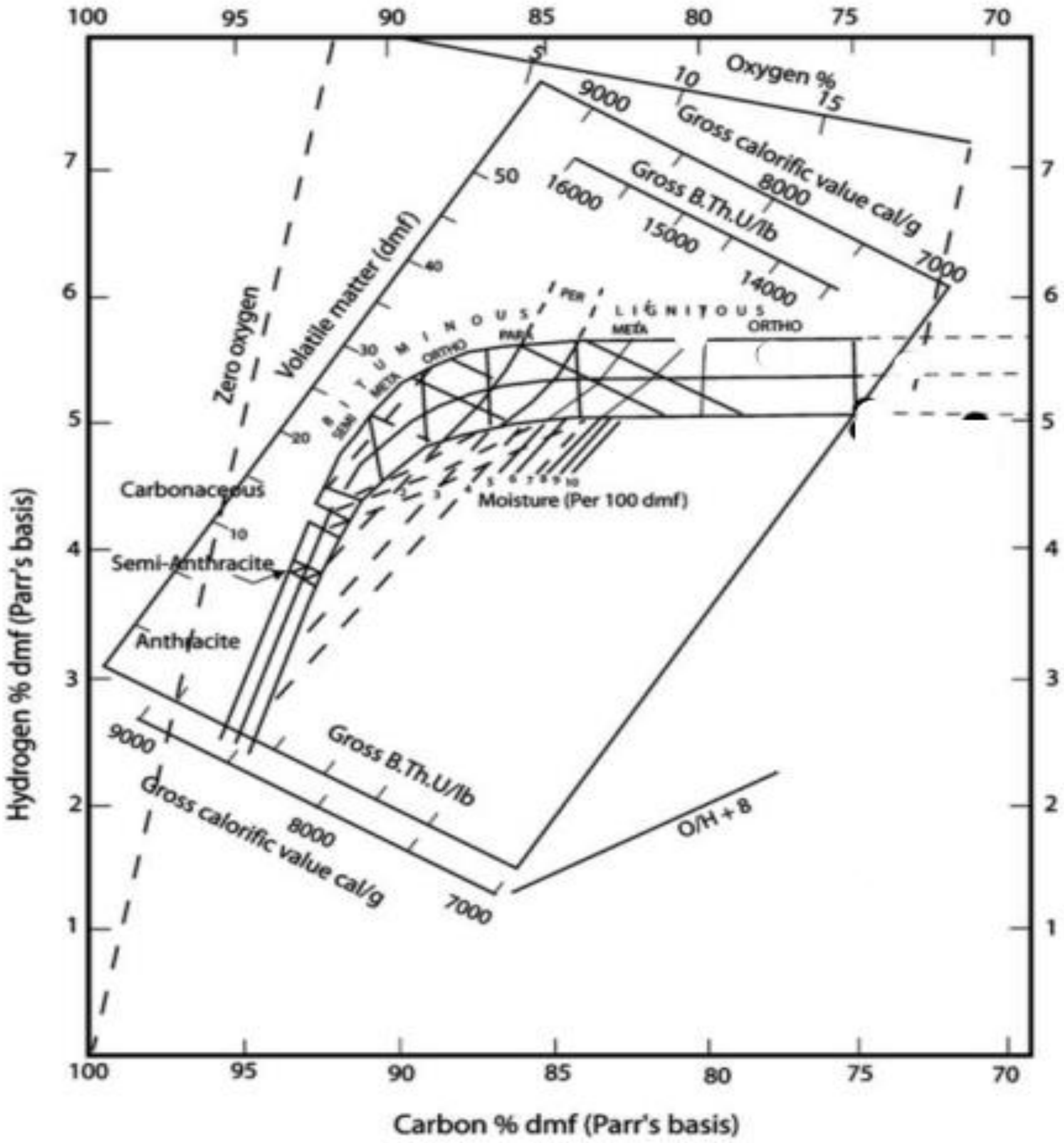
- Fixed carbon
- Volatiles
- Moisture
- Ash
- CV

Ultimate analysis

- Carbon
- Hydrogen
- Sulphur
- Nitrogen
- Moisture
- Ash
- CV

SEYLER CHART (Ultimate analysis)

Clarence Seyler (1866 - 1959), Chemist and Public Analyst.



PROPERTIES OF COAL

Proximate analysis of steam coals:

Mine	Bedwas (Sth Wales)		Blidworth (Notts)		Lilleshall (Salop)		Ffos-y-Fran open cast (South Wales)
	As rec'd	Dry	As rec'd	Dry	As rec'd	Dry	
CV (MJ/kg)	32.68	33.05	29.21	31.69	29.44	31.72	30*
Fixed Carbon (%)	64.3	65.0	52.0	56.4	48.2	51.9	
Volatile matter (%)	26.6	26.9	35.0	38.0	39.9	43.1	
Moisture (%)	1.1		7.8		7.2		
Ash (%)	8.0	8.1	5.2	5.6	4.7	5.0	5 – 8*
Sulphur (%)	0.65	0.65	0.78	0.85	0.9	0.97	1.3 – 2.0*

Source: British Railways Performance & Efficiency Test Bulletin No3 1951

* http://www.cwfuels.co.uk/knowledge/calorific-information/
(As with all naturally mined fuels there may be slight fluctuations in the figures reported on different shipments)

PROPERTIES OF COAL

CV calculation: Dulong equation: LHV [kJ/g] = 33.8 mC + 122.3 (mH − mO/8) + 9.4 mS

Using Dulong equation to identify component heating contributions:

Bituminous coal (Ultimate analysis)				Anthracite (Ultimate analysis)			
CV (dmf)		36.63	MJ/kg	**CV (dmf)**		35.86	MJ/kg
	=	15749	BTU/lb		=	15418	BTU/lb
C =	90 wt%	30.33	MJ/kg	**C =**	94 wt%	31.68	MJ/kg
H =	4.8 wt%	6.25	MJ/kg	**H =**	3.1 wt%	4.14	MJ/kg
O =	3.7 wt%			**O =**	1.5 wt%		
S =	0.5 wt%	0.05	MJ/kg	**S =**	0.5 wt%	0.05	MJ/kg

Dulong equation comparison (using Ultimate analysis figures).

- High carbon for heat.
- Carbon greater than 90% to give high CV.
- Calorific value greater than 30 MJ/kg.

COAL SUBSTITUTE IDEAL REQUIREMENTS

Combustion requirements:

- Similar CV to coal.
- Carbon (Ultimate analysis) - 90% to 95%.
- High density - As dense as coal.
- Low volatiles – similar to anthracite (Welsh steam coal).
- Low smoke.
- Low ash.
- Low or zero moisture.

- Does not foul the boiler – free from contaminants; fusible ash, corrosive gasses.
- Does not break up with handling or combustion.
- Lumps do not break up in firebed before combustion complete.
- Easy release of volatiles.
- High surface area for carbon combustion.
- Ash falls into the ash pan and not carried over into the flue gas.
- High ash fusion temperature.

COAL SUBSTITUTE IDEAL REQUIREMENTS

Storage requirements:

- Does not degrade in outdoor, long term storage.
- Waterproof.
- Rodent proof.

General requirements:

- Carbon neutral.
- Similar price to coal.
- Available in large sizes – fist size with no fines.

- Raw material supply chain exists or can be easily created.
- Can be manufactured in existing processing plants.
- Can use current distribution systems.
- No additional waste handling – preferably no need for plastic sacks.

BIOMASS GENERAL COMBUSTION CHARACTERISTICS

Biomass is not an ideal substitute for coal.

- It has a lower CV than coal.
- It has a lower energy density.
- It contains several noxious components.

Question is: Can it be made into a suitable alternative to lump coal within a reasonable cost?

Answer: Probably; using thermal treatment to breakdown and remove the noxious components.

Biomass woody tissue mainly consists of:

- Cellulose – Approx 40%
- Hemicellulose – Approx 30%
- Lignin – Approx 30%

Besides the three main components, natural lignocellulosic materials contain a small amount of pectin, inorganic compounds, and ash.

The ratio differs from sources such as; hardwood, softwood, and crop residues.

BIOMASS GENERAL COMBUSTION CHARACTERISTICS

The analysis of wood by weight is about:
- 50 % carbon
- 6 % hydrogen
- 44 % oxygen
- 0.05–0.4 % nitrogen

Approx overall wood - C6.H12.O6

Cellulose
- Cellulose is the main substance, which makes up the cell walls and fibers of plants.
- Cellulose consists of a linear chain of glucose units, each polymer of cellulose comprises 7,000–15,000 glucose units.

Hemicelulose
- Hemicelulose is primarily in leafs and green parts of biomass.
- Hemicelluloses consist of shorter chains than cellulose – 500–3,000 glucose units.
- Hemicelluloses may be branched polymers, while cellulose is unbranched. Hemicelluloses are embedded in the cell walls of plants, sometimes in chains that form a 'ground' – they bind with pectin to cellulose to form a network of cross-linked fibres.

Leaves are composed primarily of hemicellulose and cellulose.

BIOMASS GENERAL COMBUSTION CHARACTERISTICS

Lignin

- Lignin acts as a binder for the cellulose fibers, adding strength and stiffness to the plant cell wall.
- Lignin's molecular masses exceeds 10,000 glucose units.
- Lignin fills the spaces in the cell wall between cellulose, hemicellulose, and pectin components.
- The composition of lignin varies from species to species.

Pectin

- Pectin is composed of complex polysaccharides that are present in the primary cell walls of a plant, and are abundant in the green parts of terrestrial plants.

Nutrients

Plants must obtain mineral nutrients from their growing medium.

Nutrient elements exist within soils as salts and plants absorb these elements as ions.

Nutrients can be naturally occurring or added as fertiliser.

Agronomists split the nutrient elements into macronutrients and micronutrients.

BIOMASS GENERAL COMBUSTION CHARACTERISTICS

Macronutrients:

Three main macronutrients – such as from NPK fertilizers:

- Nitrogen (N): leaf growth and stems.
- Phosphorus (P): development of roots, flowers, seeds and fruit.
- Potassium (K): strong stem growth, movement of water in plants, promotion of flowering and fruiting.

Secondary macronutrients are:

- Calcium (Ca)
- Magnesium (Mg)
- Sulphur (S)

For agricultural biomass most nutrients are added by fertilisation.

BIOMASS GENERAL COMBUSTION CHARACTERISTICS

Micronutrients:

The main micronutrients (or trace minerals) are:

- Chlorine (Cl)
- Iron (Fe)
- Boron (B)
- Manganese (Mn)
- Zinc (Zn)
- Copper (Cu)
- Molybdenum (Mo)
- Nickel (Ni)

Of occasional significance are:

- Silicon (Si)
- Sodium (Na)
- Cobalt (Co)
- Vanadium (V)

Micronutrients are present in plant tissue in quantities measured in parts per million, ranging from 0.1 to 200 ppm, or less than 0.02% dry weight.

BIOMASS GENERAL COMBUSTION CHARACTERISTICS

Nitrogen:

Fixed inorganic nitrogen compounds are required for the biosynthesis of all nitrogen-containing organic compounds such as amino acids, polypeptides and proteins, nucleoside triphosphates and nucleic acids, essential for soil fertility and the growth of terrestrial and semiaquatic vegetation.

Some bacteria and their host plants (notably legumes) can fix atmospheric nitrogen (N_2).

The main nitrogen-based straight fertilizer is ammonia (NH_3) ammonium (NH_4^+) or its solutions, including:

- Ammonium nitrate (NH_4NO_3) with 34-35% nitrogen is also widely used.
- Urea ($CO(NH_2)_2$), with 45-46% nitrogen, another popular source of nitrogen.
- Ammonium sulphate $(NH_4)_2SO_4$ is in common use as a soil fertilizer. It contains 21% nitrogen and 24% sulphur.
- Calcium nitrate with 15,5% nitrogen and 19% calcium, reportedly holding a small share of the nitrogen fertilizer market (4% in 2007).
- Calcium ammonium nitrate Is a blend of 20-30% limestone $CaCO_3$ or dolomite $(Ca,Mg)CO_3$ and 70-80% ammonium nitrate with 24-28 % nitrogen.

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BIOMASS GENERAL COMBUSTION CHARACTERISTICS

Chlorine:

Chloride fulfils many important functions in plants. Some of the roles of Cl- in plants are:

- Photosynthesis.
- Enzyme activation.

Potassium chloride KCl (muriate of potash) is the most commonly used K fertilizer in the world providing crops with two nutrients, K and Cl, essential for both plants and animals. On application to most soils, both these nutrients are readily available to crops.

Sulphate:

Potassium sulphate K2SO4. Sulphate-containing fertilizers provide most of the fertilizer S applied to soils. These materials have the advantages of supplying S primarily as a component of multi-nutrient fertilizers in a form, SO4 that is immediately available for plant uptake.

BIOMASS GENERAL COMBUSTION CHARACTERISTICS

Phosphate:

Phosphate (PO_4) is required for the production of DNA (genetic code) and ATP, Adenosine triphosphate (ATP)

- "Single superphosphate" (SSP) consisting of 14–18% P_2O_5, again in the form of $Ca(H_2PO_4)_2$, but also phosphogypsum ($CaSO_4 \cdot 2\,H_2O$).
- Triple superphosphate (TSP) typically consists of 44–48% of P_2O_5 and no gypsum.
- A mixture of single superphosphate and triple superphosphate is called double superphosphate. More than 90% of a typical superphosphate fertilizer is water-soluble.

High potassium and chlorine contents in many biomasses are potentially harmful elements with regard to corrosion.

COMBUSTION OF BIOMASS

As with coal combustion:

Primary air

- Combustion of carbon to carbon monoxide CO.
- H_2O evaporation.
- Pyrolysis and release of VOC.

Secondary air

- Combustion of CO.
- Combustion of VOC.

Complete combustion would consume all the VOC to give; CO_2, H_2O, O_2, N_2 + inorganic acid gases and NO_x.

For the inorganic “nutriant” components:

The thermal breakdown of nitrogen components within the biomass produces Ammonia NH_3 and Hydrogen cyanide HCN, which should all be burned above the firebed.

COMBUSTION OF BIOMASS

Noxious components, chlorine, sulphur, phosphorus, etc. in the VOC should be fully oxidised and released as vaporised salts and some acids:

- Hydrochloric acid HCl
- Sulphuric acid H_2SO_4
- Sulphurous acid H_2SO_3
- Phosphoric acid H_3PO_4
- Nitric acid HNO_3
- Nitrous acid HNO_2

Stack emission temperature should therefore be well above any acid gas condensation temperatures.

Corrosive components – particularly chlorine (Cl)

One of the major problems in biomass boilers is corrosion, mainly from burnt fuels containing alkali metals, chlorine and other corrosive elements.

Many types of biomass except wood, (but including miscanthus biomass) have a relatively high chlorine amount.

Note: It is reported that the chlorine amount in miscanthus reduces by approximately 95% when it is torrified at 350°C

COMBUSTION OF BIOMASS

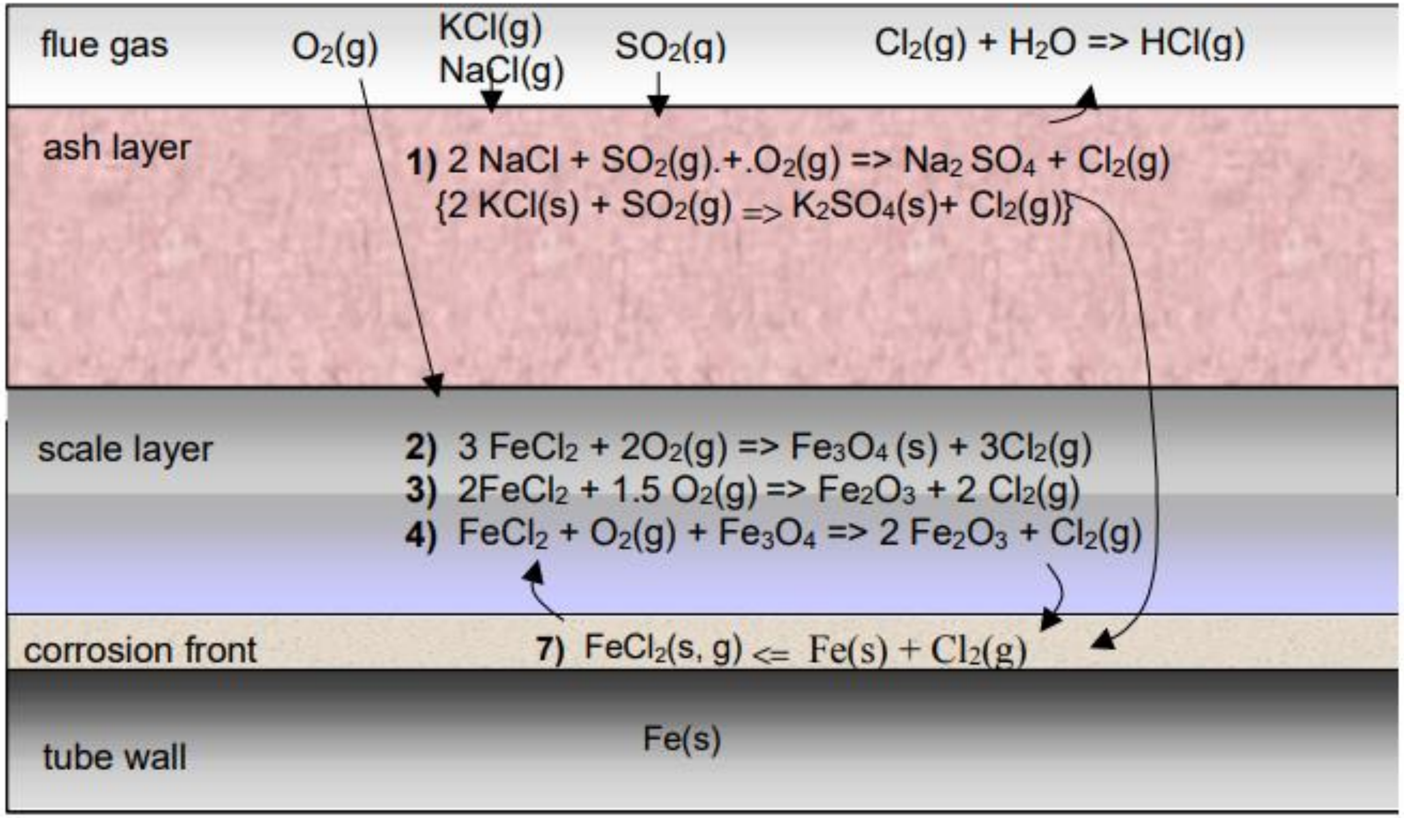


Figure 3: Principles of the corrosion mechanism by active oxidation

BIOMASS COMBUSTION ISSUES

Incomplete combustion:

CO + unburned hydrocarbons (including HCN)

As a measure of the VOC from biomass incomplete combustion, studies of wood smoke give:

- 48 different acids – Principally Acetic acid (13.9% in one sample)
- 22 different alcohols Principally Methanol (13.5% in one sample)
- 75 different phenols - Principally Guiacol (dimethoxy phenol) (9.2% in one sample)
- 131 different carbonyls (ketones) Principally Hydroxy, butanone (5.2% in one sample)
- ‘carbonyls (aldehydes) Principally Dimethoxy benzaldehyde (0.8% in one sample)
- ‘enols - Principally Cyclotene (hydroxy-methyl-cyclopenten) (3.1% in one sample)
- 22 different esters.
- 46 different furans.
- 16 different lactones.

Many of these are carcinogenic.

All biomass feedstocks are different and will give different ratios of carbon, VOC and corrosive gasses.

BIOMASS COMBUSTION ISSUES

The autoignition temperature of most biomass VOC is in the range 500°C to 620°C so all should be burned to CO2 and H2O given:

- Sufficient secondary air.
- Continuous exposure to high temperature.
- Sufficient firebox residence time.

Large firebox volume, high temperature and long residence time are required to combust most VOC.

Gas producer combustion systems would be the most efficient.

- Porta Gas Producer Combustion System (GPCS).
- Kirklees Light Railway GPCS.

Normal locomotive fireboxes do not have sufficient residence time, at high temperature, to ensure complete combustion of large amounts of VOC – Less than 0.5 seconds at full load.

Dioxins and furans are produced if chlorides present (waste incineration unit operating procedures require 2 seconds at greater than 850°C to breakdown dioxins and furans).

❖ Best strategy for the substitute fuel would be to minimise VOC in the briquette material.

BIOMASS COMBUSTION EMISSIONS

The UK National Air Pollution Control Programme (2022) sets out the aims to meet its 2020 and 2030 emissions reduction commitments for five pollutants:

- Nitrogen oxides NOx
- Ammonia NH3
- Sulphur dioxide SO2
- non-methane VOC
- Particulate matter

Particulates – particularly micro particulates PM2.5
Particulate size regulations - What is the safe level of PM2.5 in the UK?

- Most studies indicate PM2.5 at or below 12 µg/m3 is considered healthy with little to no risk from exposure.
- In September 2021, WHO published updated Air Quality Guidelines. 2 The new guideline for annual average concentrations of PM2.5 is 5 µg/m3.
- The Environmental Targets (fine particulate matter) (England) Regulations 2023 set two PM2.5 targets to be met by 2040, these require that: The annual mean concentration is 10 µg/m3 or lower.

Environment Bill and heritage attractions - Defra Press Office, 9 July 2021.
The Government understands and appreciates the important contribution that the heritage sector, including steam railways, makes to our national culture. The smoke emission measures in the Environment Bill will not apply to emissions from steam trains. 9 Jul 2021

BIOMASS COMBUSTION ASH

Biomass is generally very low ash.

Ash may include:

- SiO_2
- K_2O
- K_2CO_3
- Na_2O
- Na_2CO_3
- $Na_2O \cdot 2SiO_2$
- CaO
- $CaCO_3$ (calcite)
- $CaSO_4$ (anhydrite)
- Fe_2O_3

Ash fusion temperature:
The ash fusion temperature of biomass can vary widely depending on the type of biomass, its composition, and the conditions under which it is burned.

Ash fusion may be an issue; clinkering, adhesion to firebars, birdsnesting..

BIOMASS COMBUSTION ASH

It is reported that generally, the ash fusion temperature of biomass is lower than that of coal, with most biomass ashes having fusion temperatures in the range of 600°C to 900°C.

Carbonates, such as K_2CO_3 and Na_2CO_3, can form solids with melting temperatures of 600°C and above.

Sodium reacts with ash minerals (such as silica) to form molten silicates with low melting temperatures.

CaO in ash can combine with other minerals at high temperatures to form eutectics, such as Rankinite ($Ca_3Si_2O_7$).

Alkali oxides, such as K_2O and Na_2O may react with SiO_2.

Chlorine and potassium in biomass ash are reported to lower the ash melting point considerably compared to coal.

BIOMASS SOURCES

Biomass:
Commercial biomass boilers use various fuels, such as; wood pellets, straw, sawdust, cardboard.
Typical biomass feedstocks:

- Energy crops – Miscanthus.
- Agricultural waste – straw, coconut shells.
- Forestry waste.
- Sawmill waste – offcuts, sawdust.
- Initial product cost.
- High transport cost.

Other potential biomass sources could be:

Municipal green waste collection and tree surgeon residue chipping:

- Municipalities pay about £100 per ton for general waste disposal.
- High moisture content.
- High collection cost.

Waste hydrocarbon materials:

- Scrap timber.
- Waste cardboard and paper.
- Scrap rubber and non chloride plastics.

BIOMASS SOURCES

Scrap timber / recycled wood such as building site waste and broken pallets:

- Small negative cost to remove from sites building etc. – about £400 per lorry load.
- Would normally be low moisture.
- Could include waste cardboard.
- Nails and other inorganic material would need to be removed after pyrolysis.

Current scrap timber reclamation:

- Sold for reuse as timber.
- Sold for chipping to make into chip board (particle board) and particle moulded products (pallets etc).

Wood Recyclers' Association (WRA)
Website https://woodrecyclers.org give details about waste wood recycling and reprocessing in the UK.

Scrap tyres / rubber and plastics:
A lot of research and technical papers into pyrolysis of scrap tyres and waste plastics:

- Particularly for liquid and gaseous fuel production.
- Carbon char for carbon black.
- Tyres are costly to dispose of so the pyrolysis raw material is negative cost.

BIO CARBON PRODUCTION

Biomass thermal modification to produce a carbon source:

There are many processes for the thermal modification of biomass:

- Charcoal burning for metallurgical charcoal since the bronze age.
- Closed kiln and retort heating to produce tar and creosote are old processes.
- Torrification currently used to produce thermally modified timber and biochar (with significant volatiles content)
- Pyrolysis with the principal object of creating; commercial charcoal, liquid biofuels and fuel gas.

Thermal treatments:

- Break down the long C-H-O + N chain molecules.
- Increase energy density.
- Reduce or eliminate VOC.

Biochar from high temperature pyrolysis can be very high carbon content.

Biomass thermal treatments tend to drive off contaminants such as N and Cl.

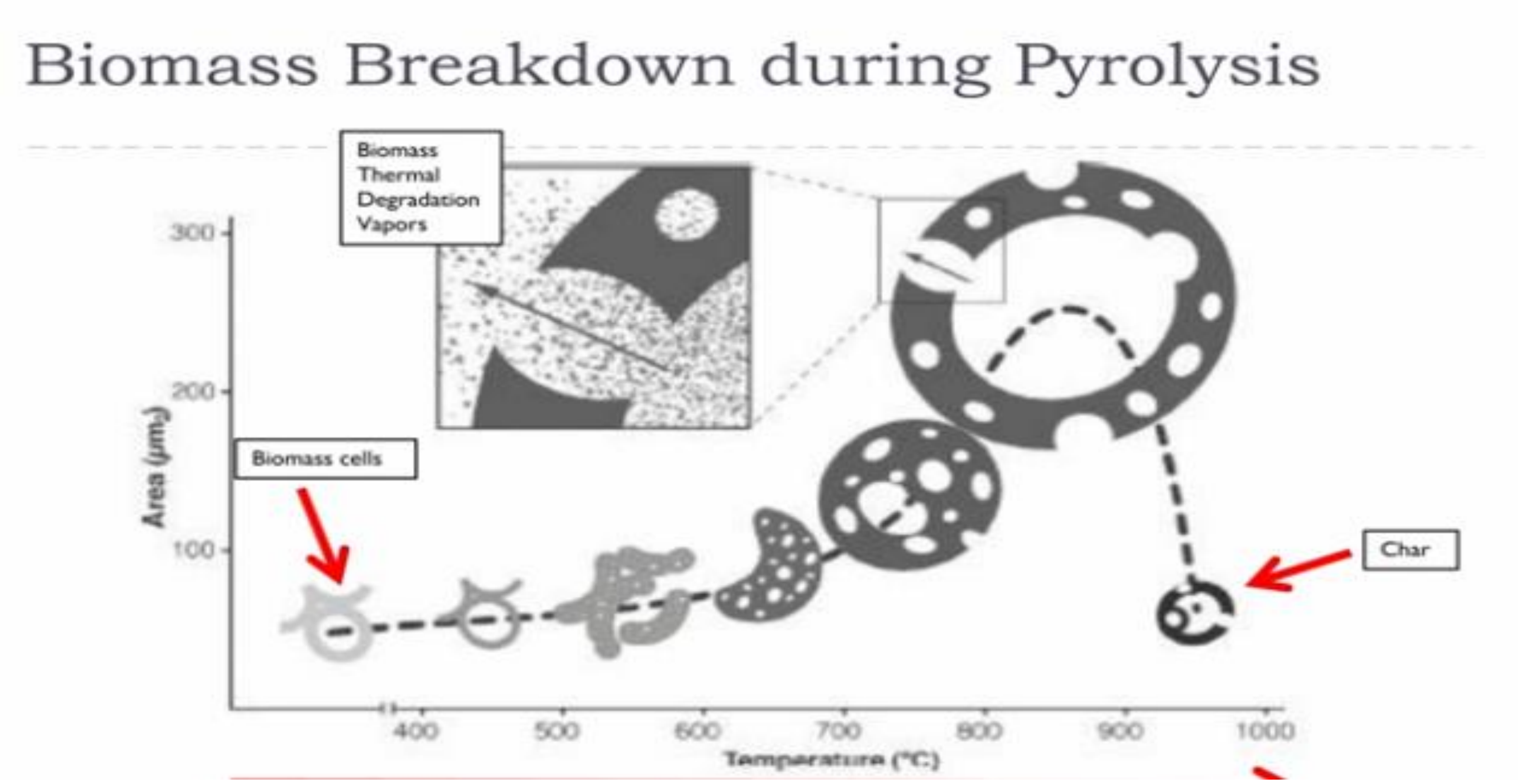
BIO CARBON PRODUCTION

Thermal decomposition process during pyrolysis:

- Free moisture release at 100°C
- Bound moisture release at 150°C
- Between 200°C and 280°C, endothermic, low temperature pyrolysis (thermal degradation of organic compounds) takes place; methanol, acetic acid, and other oxygenated VOCs are released during this stage.
- Significant emissions of CO_2 and CO from the breakdown of hemicellulose and cellulose also occur during endothermic pyrolysis.
- Between 280°C and 500°C, exothermic pyrolysis occurs; a combustible mixture of VOCs and tars are emitted.
- Above 500°C to about 1000°C, gives a reduction in the small amount of remaining VOCs.

- Hemicellulose decomposition 200°C - 260°C
- Cellulose decomposition 240°C - 350°C
- Lignin decomposition 280°C - 500°C

BIO CARBON PRODUCTION



BIO CARBON PRODUCTION

Pyrolysis time and temperatures need to be regulated to maximise carbon yield.

Treatment at temperatures from 250°C to 350°C is called torrification.

Pyrolysis temperatures are normally in the range 350°C to 600°C

Gas works distillation temperatures:

- Bituminous coal was heated to a temperature of about 400°C
- Coal softens and coalesces, giving off water vapour, rich gas and tar.
- The temperature was raised to 1,000°C
- Remaining volatile matter, almost entirely driven off leaving coke residue.

Gas works coke was almost 100% carbon.

BIO CARBON PRODUCTION

Torrification:

Torrification - lower temperature range pyrolysis to convert biomass to a char-like substance.

Heating to temperatures in the range 250°C to 350°C in an inert atmosphere.

Bio char made by torrification at 300°C is brown, soft and friable, and will ignite at about 380°C

Bio char made at higher temperatures (pyrolysis) it is hard and brittle, and does not ignite until heated to about 700°C

Torrification produces a dry product, and reduces or eliminates the potential for organic decomposition.

Torrification combined with densification creates an energy-dense fuel carrier of 20 to 21 GJ/tonne (LCV).

Torrification reduces the amount of volatiles - the chlorine amount in miscanthus reduces by approximately 95% when torrified at 350°C

BIO CARBON PRODUCTION

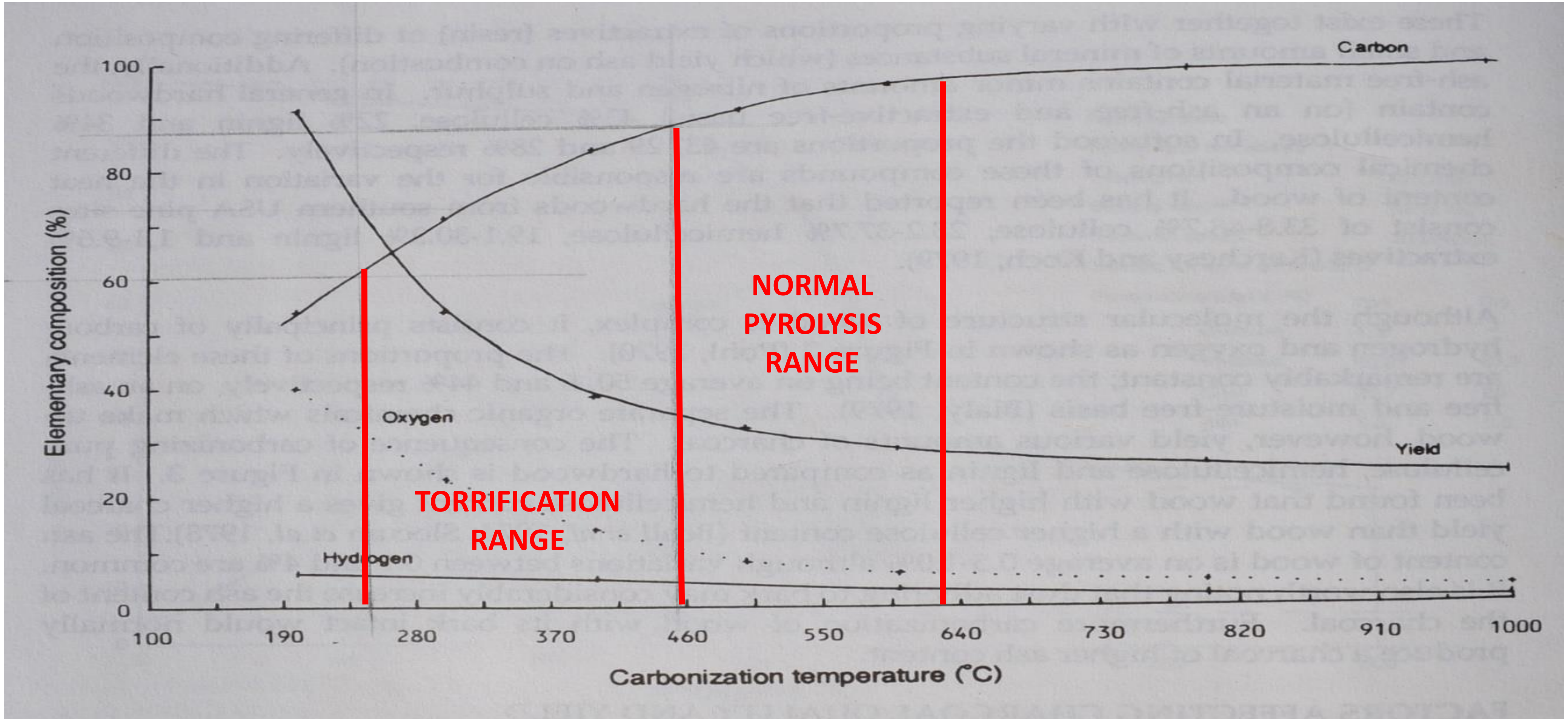


Figure 2 **Elementary composition and yield of charcoal in relation to carbonization temperature (Pohl, 1970)**

BIO CARBON PRODUCTION

Biochar has a very wide range of compositions depending on the carbonisation temperature:

- For a carbonisation temperature of 250°C (torrified biomass): C = 60% and CV = 20MJ/kg.
- For a carbonisation temperature of 450°C (typical barbeque lump charcoal): C = 87% and CV = 31MJ/kg.

The specific yield from pyrolysis is dependent on process conditions such as temperature, residence time, and heating rate.

Pyrolysis of the feedstock at 600°C would result in a lower char yield from the initial biomass input, and would make a final fuel product more expensive.

Pyrolysis of the feedstock at 600°C would drive off most the VOC and inorganic gases, including HCN.

BIO CARBON PRODUCTION

Biomass pyrolysis products:

Non condensable gases:
- H_2
- CH_4
- CO
- N_2
- CO_2

Condensable liquids:
- Water
- Pyroligneous acid:
  - Acetic acid - CH_3COOH
  - Acetone - $(CH_3)_2CO$
  - Methanol - CH_3OH
- Terpenes
- Wood tar

Terpenes are a class of natural products consisting of compounds with the formula $(C_5H_8)_n$ for $n \geq 2$.
Terpenes comprise more than 30,000 compounds, these unsaturated hydrocarbons are produced predominantly by plants, particularly conifers. Terpenes are classified by the number of carbons: monoterpenes (C10), sesquiterpenes (C15), diterpenes (C20).

BIO CARBON PRODUCTION

Biomass tar composition (major components)

- Toluene
- Phenol
- Naphtaline
- 4-Methylguaiaxol
- Guiacol
- Indene
- Phenantrene
- Fluoranthene
- Pyrene

Pyrolysis heating rate:

Slow pyrolysis can produce substantially more char (≈35%)

Increasing heating rate leads to a decrease of biochar yield.

Pyrolysis plants can use the syngas output and yield 3–9 times the amount of energy required to run.

For typical inputs, the energy required to run a "fast" pyrolyzer is approximately 15% of the energy that it outputs.

BIO CARBON PRODUCTION

Kiln and retort pyrolysis:

- Very old technology.
- Archaic charcoal production.
- Many retort plant configurations.
- Cyclic plants with fresh batch heating from previous batch gasses.

Modern pyrolysis plant:

- Package batch production plants – long heating and cooling times.
- Continuous (screw feed) production plants – tend to be larger than batch plants.
- Continuous charge gasifiers.
- Fluidised bed systems.
- Fluidised bed systems which include catalysts (for plastics waste and scrap tyres).

HydroThermal Carbonization (HTC) process

- Green waste.
- Sewage sludge.
- Temperatures 180°C to 250°C

BIO CARBON PRODUCTION

SMALL PACKAGED BATCH PYROLYSIS PLANT

BIO CARBON PRODUCTION

Thermally modified wood:
Thermally modified wood is engineered wood that has been modified by a controlled pyrolysis process of wood being heated to (> 180°C) in an oxygen free atmosphere.

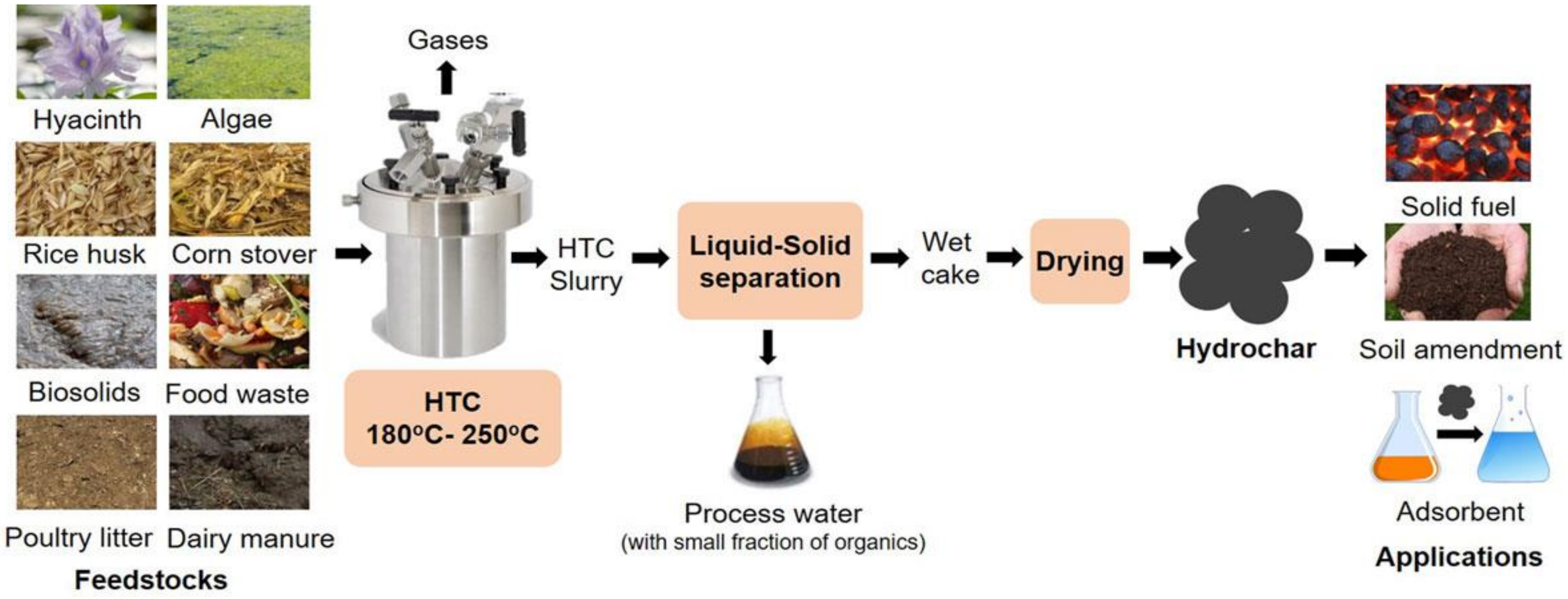
The process changes to the chemical structures of wood's cell wall components lignin, cellulose and hemicellulose which decreases its hygroscopy and thus increases dimensional stability.

Low oxygen level during processing prevents the wood from burning at the high temperatures. Several different technologies use different media including nitrogen gas, steam and hot oil. All processes degrade strength and toughness of the treated wood to some degree.

HydroThermal Carbonization:
HydroThermal Carbonization (HTC) also referred to as "aqueous carbonization at elevated temperature and pressure"

- Thermochemical process by which biomass is treated in aqueous environment.
- Temperatures of 180–250°C and self-generated pressure.
- Produces solid fuel as hydrochar.
- Wide range of organic wastes such as garbage, bio solids, agro residues and organic wastes.
- Reported to produce high biochar yields from low quality, high moisture biomass.

BIO CARBON PRODUCTION



180°C = Saturated steam pressure of 9barg (130psig)
250°C = Saturated steam pressure of 37barg (540psig)

BRIQUETTE MANUFACTURE

Briquette components:
- Carbon – for high heat.
- Volatiles/accelerants – for lightability and firebed heat maintenance.
- Binders.
- Fillers.
- Mould release compound.

Bio briquette requirements:
- Good calorific values.
- Minimise volatiles.
- High VOC release rates.
- Maintain structure in the firebed.
- Provide a large surface area for carbon combustion.
- High heat output rates.
- Low moisture.
- Low ash.

Influences:
- Carbon component mixture – pyrolyzed plus torrified material.
- Choice of binder(s).
- Moulding pressures.

BRIQUETTE MANUFACTURE – POTENTIAL BINDERS

Wide range of blinders available - Many binder vendors advertising on the internet.

Binder cost and required overall weight % required are significant to the final briquette product cost.

Binder required characteristics - Should be:

- Non fossil origin.
- Strong for mechanical handling.
- Resistant to thermal degradation.
- Will release gas during combustion without the briquette breaking up prematurely.
- Minimal effect on the heat release and combustibility of the carbon content.
- Does not produce noxious or corrosive emissions.
- Resistant to weathering.
- Readily available and low cost.

Historically used binders for coal fines briquettes:

- Petroleum asphalt.
- Gas works tar (pitch).
- Clay.

BRIQUETTE MANUFACTURE – POTENTIAL BINDERS

Binder options - Currently used binders for BBQ and 3rd world heating briquettes:

Organic - most not water resistant

- Starch.
- Modified starch.
- Molasses - attractive to rodents.
- Gum Arabic.
- Guar gum.
- Algae.
- Phenolic resins.
- Gelatin.
- Wood tar.
- Crude glycerin (biodiesel manufacture biproduct).
- Waste paper pulp (lignophosphate).
- PVA (Polyvinyl alcohol).

BRIQUETTE MANUFACTURE – POTENTIAL BINDERS

Inorganic - normally not combustible therefore ash forming:

- Clay - notably bentonite clays (an absorbent swelling clay).
- Cement.
- Plaster (including plaster of Paris).
- Hydrated lime.
- Sodium silicate.
- Sodium humate.

Compound - Mixture of several different binders:

- Starch + bentonite clay is popular.
- Many other combinations.

Quote from one researcher "compound binding is becoming the main direction of development of briquette binders in recent years“.

Starch
A common and inexpensive binder that can be made from corn, wheat, maize, rice, cassava, or potato. Starch is often used to make BBQ charcoal because it's natural and smokeless. However, starch doesn't perform well at high temperatures.
In general, about 4–8% of starch is needed to make the briquettes. Starch sources can be corn starch, wheat starch, maize flour, wheat flour, rice flour, cassava flour, potato starch, etc. To use the starch as a binder you must first gelatinize the starch which is added to water and heated to a sticky consistency, then adding to the mixer to be mixed with charcoal powder.

BRIQUETTE MANUFACTURE – POTENTIAL BINDERS

Modified starch, also called starch derivatives, is prepared by physically, enzymatically, or chemically treating native starch to change its properties. Modified starches are used in practically all starch applications
Carboxymethylated starches are used as a wallpaper adhesive and as textile printing thickener.
Cationic starch is used as wet end sizing agent in paper manufacturing.

Wood Tar and Pitch
Wood tar from the carbonisation process can be recovered from kilns and retorts. Tar is more liquid while pitch is more solid. Both of them require re-carbonisation to avoid the emission of heavy smoke which may generate adverse health.
Wood tar has been used as a water repellent coating for boats, ships, sails, and roofs since prehistoric times. In Scandinavia, it was produced as a cash crop.
Distillation of wood tar to 270C is advised by one source, to ensure sufficient stability in the firebed, while retaining flexibility to resist mechanical handling breakage.

Bioasphalt
Bioasphalt is an asphalt alternative made from non-petroleum based renewable resources. These sources include sugar, molasses and rice, corn and potato starches, natural tree and gum resins, natural latex rubber and vegetable oils, lignin, cellulose, palm oil waste, coconut waste, peanut oil waste, canola oil waste, dried sewerage effluent.
As a binder it can provide enough strength to briquettes at a 2% addition. Briquettes made with bioasphalt have a good reduction rate and low activation energy.

BRIQUETTE MANUFACTURE – POTENTIAL BINDERS

Polyvinyl alcohol (PVOH, PVA, or PVAl) is a water-soluble synthetic polymer. It has the idealized formula $[CH_2CH(OH)]_n$. It is used in papermaking, textile warp sizing, as a thickener and emulsion stabilizer in polyvinyl acetate (PVAc) adhesive formulations, in a variety of coatings, and 3D printing.

Gum Arabic
Gum Arabic, also known as acacia gum, is a natural gum harvested from the acacia tree, which is very common in the African Sahel, especially Senegal, Sudan, Somalia etc. Gum Arabic is successfully being used.

Molasses
Molasses is a by-product of the sugar industry. Briquettes bound by molasses burn well, but have an unpleasant smell during combustion. To avoid this, thermal treatment can be applied before using the briquette, which is also called "curing".

Clay
A briquette can contain about 15% of clay. Clay does not add to the calorific value of the briquette. If too much clay is added, the briquette will burn poorly or not at all. And, the clay will turn into ash after burning, which blocks the passage of radient heat, resulting in the loss of calorific value of the charcoal.

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BRIQUETTE MANUFACTURE – OTHER ADDITIVES

Besides the binding material, other additives are often added during manufacture to aid combustion of briquettes.

Accelerants

Compacted briquettes may not be able to absorb sufficient oxygen for faster combustion due to compaction.
Sodium nitrate gives out oxygen when heated, so can be used as an ignition aid for briquettes, helping the briquettes to light faster. About 3-4% of sodium nitrate is needed for briquetting.
Sawdust burns quickly and is also as ignition aid. The amount of sawdust needed is about 10-20%.

Fillers

Fillers are added to briquettes to increase their weight, density or volume, which can lower production cost of the manufacturer. Fillers add no energy value. It only adds ash content. Using filler can slow down the burning rate of briquettes, but with too much filler, the briquettes will be of poor quality. Fillers must be cheaper than the charcoal fines. Cement can be used but it is expensive. Clay is cheap and can be used as filler. Sandy soil is ideal a filler for it is very common in most areas.
Ash-whitening Agent - White ash colour looks nicer and acts as a signal that BBQ briquettes are ready to cook on. A 2-3% lime, limestone or calcium carbonate is sufficient to make the ashes turn white. They are not heat fuels but can lower the burning rate to make the briquettes burn longer.

Press Release Agent

Borax or sodium borate is used in small amounts to help briquettes release from the manufacturing presses. It is not necessary to use this press release agent if you are using simple press or manual press. It is only necessary when using a high speed and high pressure briquette machine.

BRIQUETTE MANUFACTURE – PROPOSAL FOR HERITAGE STEAM

Carbon – from pyrolised scrap timber.
Volatiles/accelerants – from torrified scrap timber.
Binder – composite (maybe mixture of starch/bentonite clay/distilled wood tar).
Fillers – not used.
Moulding pressure - set to give mechanical strength but not constrict VOC release.

Issues to be resolved:

- Selection of suitable composite binder – Must provide good resistance to breaking up in the firebed.
- Must allow fissures to be created for gas release without briquette break-up.
- Must provide sufficient surface area required for quick carbon combustion.

Must be free (or very low) of Na, K, Ca, Si, N, Cl, S.

Possible VOC release paths:

- Wood fibres - crushed wood.
- Chopped straw.

Briquette binder needs to be waterproof or distribution in 25 kg plastic bags would be required.

Product could be marketed with different mixes:

- Normal high temperature operation mix - 95% Pyrolysed Carbon + 5% Volatiles.
- Light-up mix with higher volatiles - 80% Pyrolysed Carbon + 20% Volatiles.

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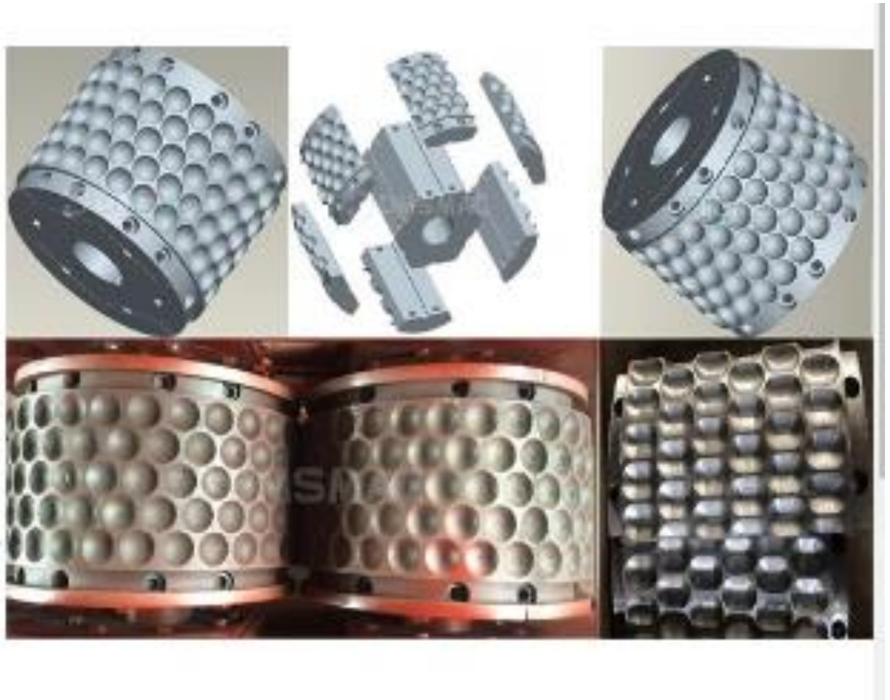
BRIQUETTE MANUFACTURE – MOULDING MACHINES

Large number of briquette machine suppliers.

Most have adjustable moulding pressures.



BRIQUETTE MANUFACTURE – PROCESS OUTLINE

Process outline:

- Transportation of feedstock.
- Shredding of feedstock.
- Torrifying/pyrolysing of feedstock.
- Crushing to carbon powder.
- Removal of tramp metals (nails etc.).
- Mixing the carbon stock and accelerants with the binder.
- Briquetting.
- Drying/carbonising.
- Bagging – if required/selected.
- Storage.
- Transportation.

CPL Homefire - How We Make Homefire Ecoal
https://www.youtube.com/watch?v=mgSMC3ucuhc

BRIQUETTE TESTING

The briquettes produced should be analysed for:

- Fixed carbon.
- Volatile Matter.
- Inorganic salts – particularly potentially corrosive components.
- Moisture content.
- Ash content and ash characteristics.
- Calorific value.

- Hardness and Toughness – Universal Testing machine (UTM).
- Density – equivalent to coal 1.1 – 1.4 – can be increased by increasing forming pressure.
- Cohesion and strength Test - Rotating Drum.
- Retention of shape in the fire and release of volatiles without breaking up.
- Weathering Resistance – moisture absorbance.
- Resistance to fungal and rodent attack.

Proximate chemical analysis

Proximate analysis can be made by heating the sample until it decomposes successively into three of the four complex items of the proximate analysis. The test laboratory is provided with a sample grinder, a muffle furnace with temperature control and indicating pyrometer, a thermostatically regulated drying oven, crucibles, desiccators jar, and analytical balances.

BRIQUETTE TESTING

Moisture Content
Samples are weighed and placed in the shallow crucibles in a 103 ± 2°C oven for three hours, then removed to a desiccator for cooling and reweighing. The percent moisture contained is the loss of weight of the sample divided by the net weight of the original sample in the crucible.

Volatile Combustible Matter
The samples are placed in deep crucibles with lids and weighed. These are inserted in a 900°C muffle furnace for 6 min, then removed, cooled in a dessicator and reweighed. The loss of weight of the sample in this instance is due to both moisture and volatile which were driven off. Moisture having been previously determined, volatile can be calculated on dry basis.

Ash Content
Samples are heated in a 750°C oven for six hours, then removed, cooled in a dessicator, and reweighed. The percent ash content is the weight of the sample remaining divided by the net original weight.

Fixed Carbon
The percent fixed carbon is considered to be the difference between 100% and the sum of the percentages of volatile matter and ash content.

Crushing strength
Crushing strength can be tested using a Universal Testing machine (UTM). This test will determine the maximum allowable force that the sample briquette can withstand.

CURRENT BS EN STANDARDS FOR BIOFUELS

ISO BS EN 17225-1 to 8:2021(en) - Solid biofuels — Fuel specifications and classes
Part 1 - General requirements
Part 3 - Graded wood briquettes
Part 7 - Graded non-woody briquettes.
Part 8 - Fuel specifications and classes
ISO BS EN 14780, Solid biofuels — Sample preparation
ISO BS EN 16948, Solid biofuels — Determination of total content of carbon, hydrogen and nitrogen
ISO BS EN 16967, Solid biofuels — Determination of major elements — Al, Ca, Fe, Mg, P, K, Si, Na and Ti
ISO BS EN 16968, Solid biofuels — Determination of minor elements
ISO BS EN 16994, Solid biofuels — Determination of total content of sulfur and chlorine
ISO BS EN 17828, Solid biofuels — Determination of bulk density
ISO BS EN 17831-2, Solid biofuels — Determination of mechanical durability of pellets and briquettes
ISO BS EN 18122, Solid biofuels — Determination of ash content
ISO BS EN 18123, Solid biofuels — Determination of the content of volatile matter
ISO BS EN 18125, Solid biofuels — Determination of calorific value
ISO BS EN 18134-2, Solid biofuels — Determination of moisture content
ISO BS EN 18847, Solid biofuels — Determination of particle density of pellets and briquettes
ISO BS EN 21945, Solid biofuels — Simplified sampling method for small scale applications
ISO BS EN 21404, Solid biofuels — Determination of ash melting behaviour

CONCLUSION

Biocoal briquettes could be a feasible coal substitute if they had:

- High carbon for heat.
- Minimum VOC - because of insufficient firebox residence time for volatiles combustion.
- Sufficient VOC for lighting and combustion stability.
- Good VOC release in the fire bed without breaking up.
- High heat release rate from the carbon.
- Good strength/stability in the fire bed and for bunkering/charging.

Issues to be resolved:

- Selection of suitable binders - Providing resistance to breaking up during handling and in the firebed.
- Providing sufficient surface area required for quick carbon combustion.
- Eliminating inorganic corrosives, and in particular chlorides.

Possible issues:

- Micro particulates in smoke may be an issue.
- Depending on binder used 25kg plastic bags may be required if briquettes are not weatherproof.

CONCLUSION

Biomass would need to be pyrolysed to remove moisture, most of the volatiles and most (all) inorganic corrosives.

Could use a mixture of; high carbon pyrolysed char, mixed with a proportion of torrified char plus a composite binder.

Very efficient production would be required to maintain comparable price with coal (currently about £450 per tonne).

- Price will depend on cheap carbon source and choice of binder.
- 30,000 tonnes per annum is a relatively small operation for specialised production.

Two different products could be marketed:

- Low volatiles/low smoke “operating mix”.
- Higher volatiles “light-up mix”.

Final product must be competitive against the alternative of conversion to oil firing and operation with biodiesel.

FURTHER RESEARCH

There is a huge amount of literature and research papers on biomass pyrolysis and combustion issues and it would be worthwhile for any manufacturers proposing to market a product to be suitable for boilers to engage with the research institutions.

The EU-funded SmartCHP projects:
BECOOL PROJECT info@becoolproject.eu – Brazil-EU Cooperation for Development of Advanced Lignocellulosic Biofuels is coordinated by the University of Bologna, Department of Agricultural Sciences, and is carried out by a consortium of thirteen partners from seven EU countries, including universities, research institutes, industries and SMEs.
The project has started in June 2017 and will run until May 2022.

International Biomass Torrification and Carbonisation Council.
c/o Renewable Energy Hub
Franz-Josefs-Kai 13/8
1010 Vienna | Austria
office@ibtc-council.org
https://www.ibtc-council.org/
The IBTC promotes sustainably produced torrified or carbonized biomass on a global scale to efficiently replace fossil coal in all industries.

Illinois Sustainable Technology Center
1 Hazelwood Dr, Champaign, IL 61820,
+1 217-333-8940

Coalition for Sustainable Rail - Duluth, Minnesota - https://csrail.org

FURTHER RESEARCH

The Natural Resources Research Institute (NRRI) at the University of Minnesota – Duluth.
A leader in the efficient processing of cellulosic biomaterial into biocoal, has engineered torrified biomass (biocoal)

Nottingham University (have done work in conjunction with CPL).

Department of Chemical Engineering, University College London.

Department of Chemical Engineering and Biotechnology, University of Cambridge.

School of Chemical and Process Engineering, University of Leeds.

Lebnitz Institute for Agricultural Engineering and Bioeconomy, Potsdam, Germany.

Abo Akademi University, Piispankatu & Turku, Finland.

Department of Chemical Engineering, University of the Basque Country, Bilbao, Spain.

School of Energy Science, Kyoto University, Japan.

Xi’an International Joint Research Centre on Solid Waste Recycling and Utilisation, Xi’an, China.

Taiyan University of Technology, Taiyan, China.

This list could be continued for several pages!