

Energy, Waste & Resources – three sides of the same coin ?

The Royal Society of Chemistry : Environmental Chemistry Group

Fuels, chemicals and materials from waste

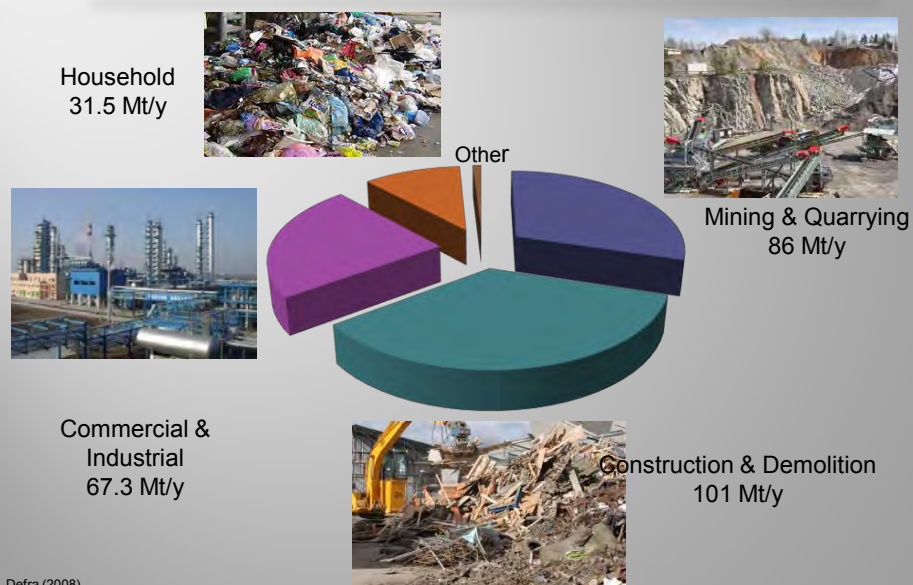
Professor Paul T. Williams

Energy Research Institute
University of Leeds



UNIVERSITY OF LEEDS

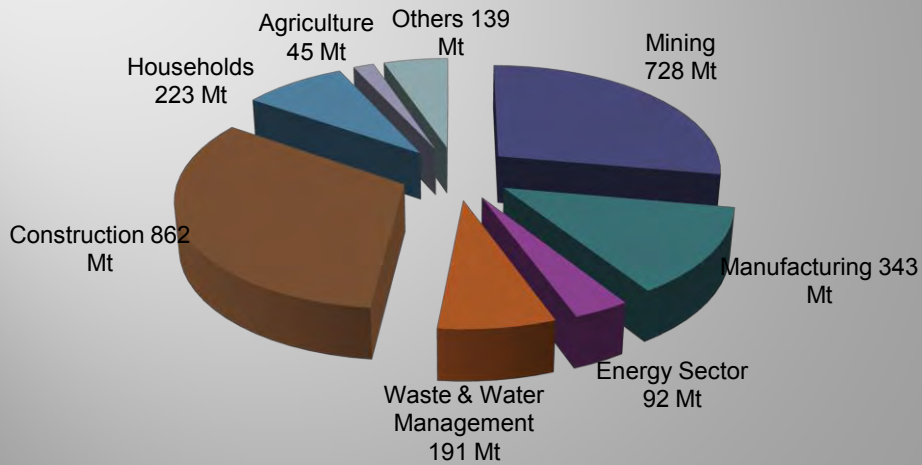
UK Waste: 288.5 Million Tonnes/Year



Defra (2008)

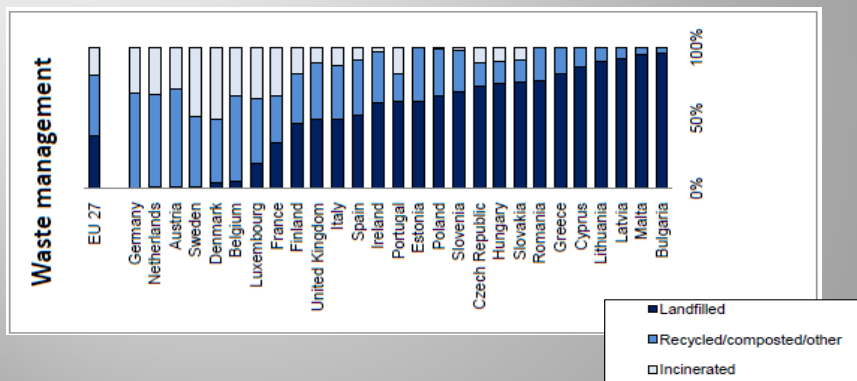
EU-27 Waste Generation

2.62 Billion Tonnes/year

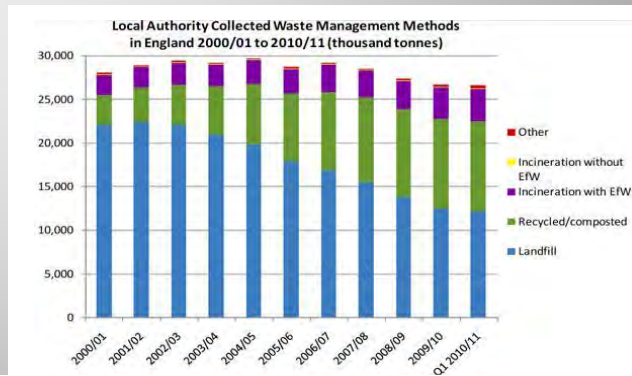


European Commission Eurostat (2008)

MSW Treatment – EU-27 (2009)



UK Household Waste: Treatment



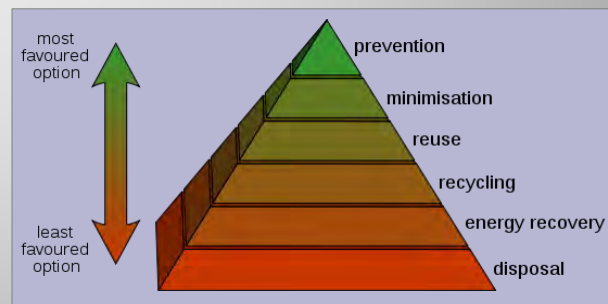
Currently;

Landfill - 49%

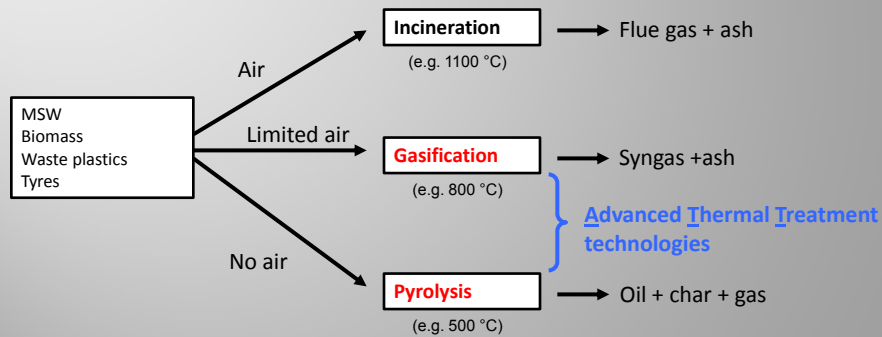
Incineration with energy recovery - 11%

Recycling/Composting - 39%

The Hierarchy of Waste Management



Thermal conversion technologies



Fuels, chemicals and materials from waste

Contents

- Pyrolysis
 - Pyrolysis technologies
 - Commercial pyrolysis plants
- Gasification
 - Gasification technologies
 - Commercial gasification plants
- Valorization of waste
 - Higher value products from wastes

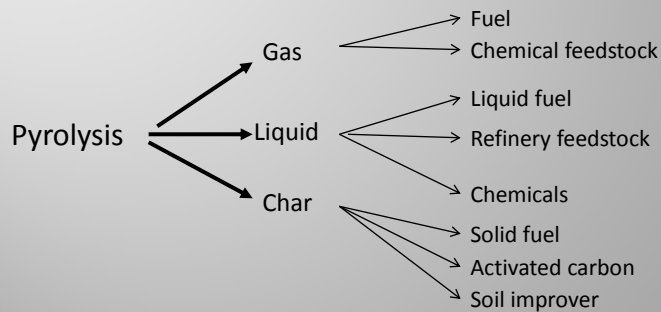
Fuels, chemicals and materials from waste

Contents

- Pyrolysis
 - Pyrolysis technologies
 - Commercial pyrolysis plants
- Gasification
 - Gasification technologies
 - Commercial gasification plants
- Valorization of waste
 - Higher value products from wastes

Pyrolysis

Pyrolysis - The thermal degradation of organic waste in the absence of oxygen to produce a carbonaceous char, oil and combustible gases



Pyrolysis: Technologies

Technology	Residence time	Heating rate	Temp (°C)	Major products
Slow pyrolysis	Hours - days	Very low	300 - 500	Charcoal
Conventional pyrolysis	5 – 30 min	Medium	400 - 600	Char, liquids, syngas
	5 – 30 min	Medium	700 - 900	Char, syngas
Fast pyrolysis	0.1 – 2 sec	High	400 - 650	Liquids
	< 1 sec	High	650 - 900	Liquids, syngas
	< 1 sec	Very high	1000 - 3000	Syngas

The terms "slow pyrolysis", "fast pyrolysis" or "flash pyrolysis" are somewhat arbitrary and have no precise definition of the times or heating rates for each process. "Fast pyrolysis" and "flash pyrolysis" sometimes are all characterized as "fast pyrolysis".

Pyrolysis reactors

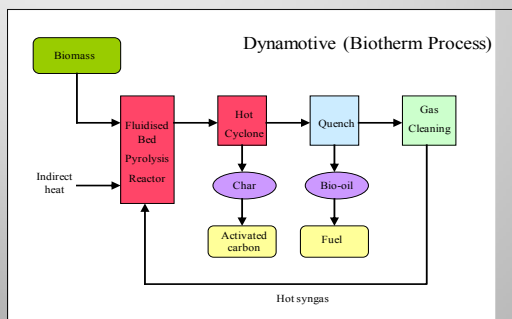
Reactor Type	Heating Method	Heating Rate
Fluidised Bed	Heated recycle gas Firetubes	High Moderate
Entrained Flow	Recycled hot sand	High
Fixed Bed	Heated recycle gas	Low
Rotary Kiln	Wall heating	Low

Biomass Fast pyrolysis: Bio-oil

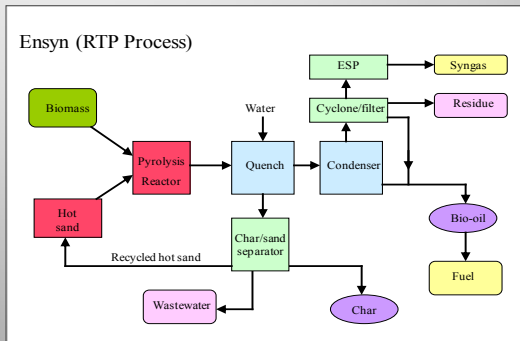
- Very high heating rates and heat transfer rate to waste materials
- Carefully controlled pyrolysis temperature (e.g. 500 °C) to maximise the liquid yield
- Short hot vapour residence times - Rapid removal of the pyrolysis vapours from the hot zone
- Rapid cooling of the pyrolysis vapours to generate bio-oil
- Bio-oil production up to 70wt%

Some Processes;

Dynamotive, Fluidised bed process



Ensyn entrained flow reactor



Bio-oil from fast pyrolysis

- Potential substitute for fuel oil and as a feedstock for production of synthetic gasoline or diesel fuel

However the bio-oil properties;

- High acidity
- Corrosive
- Poor stability
- High content oxygenated organic compounds
- Low heating value



Bio-oil Fuel Specifications

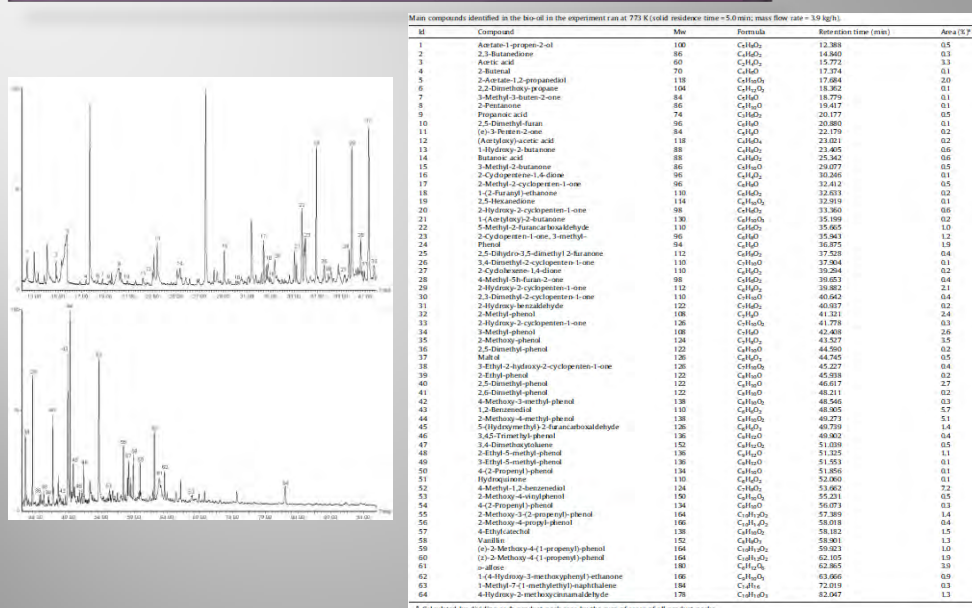
Bio-oil fuel specifications

	No2 Fuel	Ensyn bio-oil	Union Fenosa bio-oil
Feedstock	-	Hardwood	Eucalyptus
Moisture %	0	19	23
HHV MJ/kg	45	25	21
Viscosity cSt	2.7 (40 C)	1154 (25 C)	579 (25 C)
Solids %	0.05	0.65	0.94
Carbon	86.94	59.46	58.08
Hydrogen	12.48	6.22	5.97
Nitrogen	0.02	0.06	-
Sulphur	0.3	0.016	0.1
Oxygen	0.17	34.26	35.68

Composition

Organic acids	5-10 wt%
Aldehydes and hydroxyaldehydes	5 - 20 wt%
Ketones and hydroxyketones	0 - 10 wt%
Phenolics	20 - 30 wt%
Water	15 - 30 wt%

Example of compounds of bio-oil from screw kiln pyrolysis of pine wood



Bio-oil upgrading



Catalytic cracking

Catalyst, 300-500 °C



Hydrodeoxygenation

Catalyst + H₂, 70-150 °C
Pressure e.g. 40 Bar



Some Processes;

Plastics Pyrolysis



MCC Ltd., Yukaki, Japan

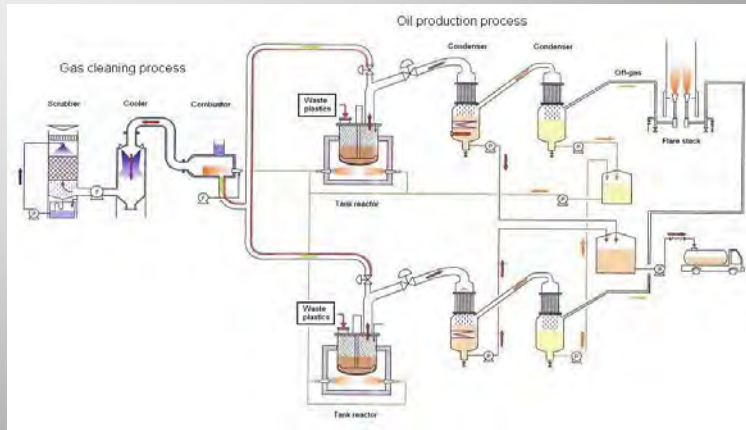


Mogami-Kiko Co., Ltd, Yamagata, Japan



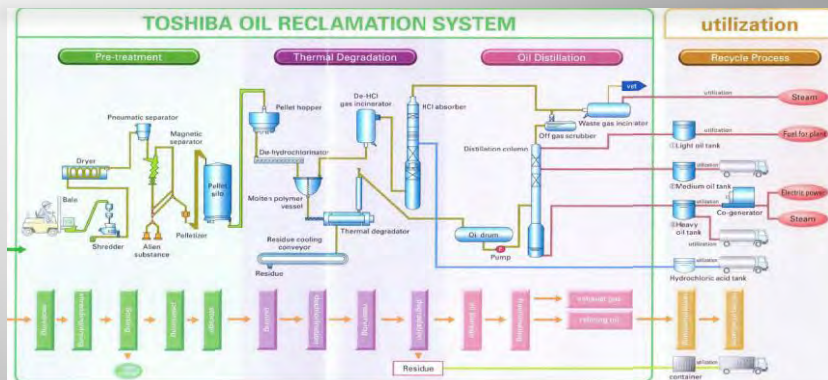
Environment System Co.,Ltd.,
Gunma, Japan

Small scale, batch pyrolysis for plastics pyrolysis



e.g. Mogami-Kiko Co., Ltd., Yamagata, Japan

Toshiba Mixed plastics pyrolysis, Sapporo, Japan



- Rotary kiln technology
- Mixed plastics from MSW
- 14,000 tpa (40 tpd – 2 lines)
- Pyrolysis oil & gas output
- HCl recovery from PVC



Splainex, Ltd, Netherlands

Pyrolysis of various wastes



- Rotary kiln technology
- Tyre, plastics, sewage sludge, MSW
- 7,000-150,000 tpa
- Pyrolysis oil & char output
- Electricity generation



Fuels, chemicals and materials from waste

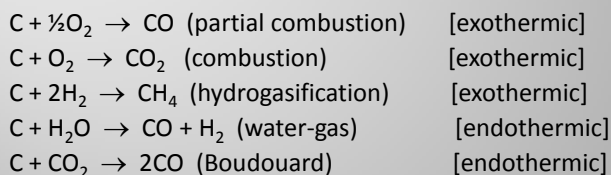
Contents

- Pyrolysis
 - Pyrolysis technologies
 - Commercial pyrolysis plants
- Gasification
 - Gasification technologies
 - Commercial gasification plants
- Valorization of waste
 - Higher value products from waste

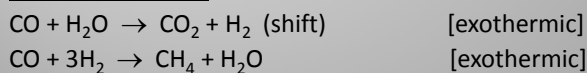
Gasification Reactions

Gasification – The partial oxidation of waste in which organic compounds are converted to a syngas comprising CO, H₂, CH₄, tar and ash

Solid-Gas Reactions



Gas-Gas Reactions



Gasification Reactor Designs

Reactor Type	Mode of contact
<u>Fixed Bed</u>	
Downdraft	Solids move ↓, Gas moves ↓, ie: co-current
Updraft	Solids move ↓, Gas moves ↑, ie: counter-current
Cross-draft	Solids move ↓, Gas moves at right angles ie: ← or →
<u>Fluidised Bed</u>	
Bubbling	Relatively low gas velocity, inert solid stays in reactor
Circulating	Much higher gas velocities, inert solid is elutriated, separated and re-circulated
<u>Moving Bed</u>	Mechanical transport of solid, usually horizontal. Typically used for lower temperature processes, ie: pyrolysis
<i>Variants</i>	<i>Multiple hearth, Horizontal moving bed, sloping hearth, screw/auger kiln</i>
<u>Other</u>	
Entrained bed	Usually there is an inert solid, has highest gas velocity of lean phase systems
Rotary kiln	
Cyclonic reactor	Good gas-solid contact High particle velocities and turbulence to effect high reaction rates

Syngas

Syngas can be used to produce Fuel, Power and Heat

However: , tar content & fine particulates, pollutants such as SO_x etc. are challenges for the subsequent process after the gasification of waste

Combustion of the 'dirty' syngas in a conventional boiler or thermal oxidizer → produce steam → power (Lower Net Efficiency 10-20%)

Cleaning of the syngas to produce a 'clean' fuel gas → power via gas engines or turbines
(Higher Net Efficiency 13-28%)

Tar

A dark, oily, viscous material, consisting mainly of high molecular weight hydrocarbons: Causes blockages, plugging and corrosion in downstream fuel lines, filters, engine nozzles etc

Methods to reduce/remove tar:

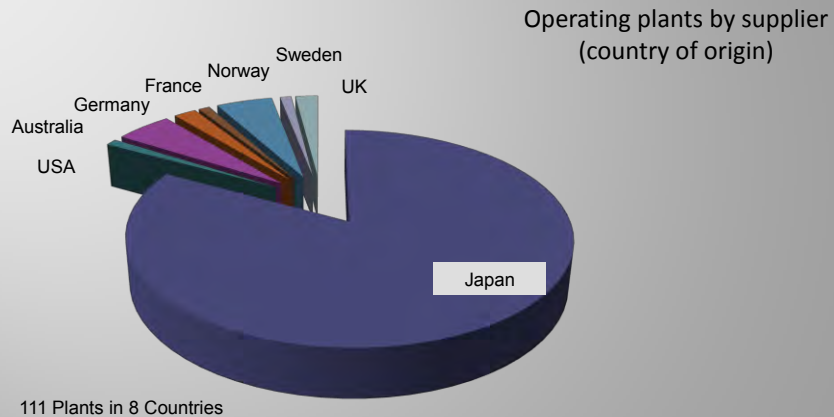
Primary:

- High-temperature gasification
- Add bed materials such as dolomite

Secondary:

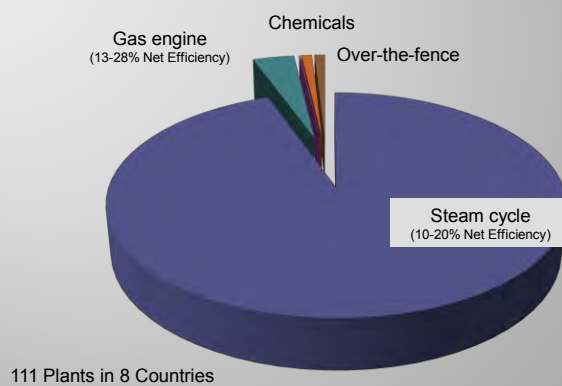
- Hot gas filters
- Wet scrubbers
- Catalytic cracking

Gasification plants processing MSW



(Source Whiting –WSP, 2010)

Syngas end-use



(Source Whiting –WSP, 2010)

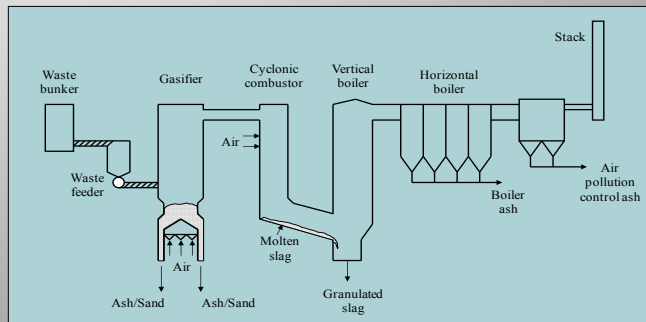
Some processes;



Ebara TwinRec Gasifier

- Combined gasification and melting process
- Fluidised bed and ash melting process
- 12 commercial plants in Japan
 - 3 mixed wastes and 9 for MSW
 - Capacities range from 19,000 to 165,000 tpa

Ebara TIFG, Kawaguchi, Japan, 2002, 125,000 Tpa



Nippon Steel

- Vertical shaft fixed bed updraft, slagging gasifier
- Municipal solid waste
- Produces 'dirty' syngas - combusted for steam for power generation
 - slag for recycling as construction aggregate
- 30 plants operating

Nippon Steel, Ibaraki, Japan, 1980, 135,000 Tpa



Mitsui R21 Process

- Gasification with high temperature combustion and slagging
- Municipal solid waste
- Mitsui and Takuma (Japanese licensees)
- 7 plants in total (largest 135 kTpa)

Mitsui R21, Toyohashi, Japan, 2002, 120,000 Tpa

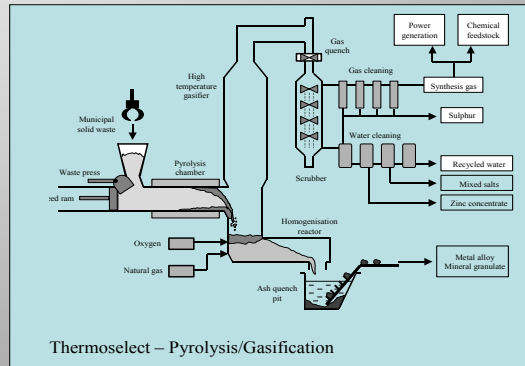
Combined Pyrolysis-Gasification



Thermoselect

- Two stage pyrolysis-gasification
- Municipal solid waste, industrial waste
- Syngas - combusted for steam for power generation
- 6 plants operating

Thermoselect, Chiba, Japan, 100,000 tpa



Fuels, chemicals and materials from waste

Contents

- Pyrolysis
 - Pyrolysis technologies
 - Commercial pyrolysis plants
- Gasification
 - Gasification technologies
 - Commercial gasification plants
- Valorization of waste
 - Higher value products from wastes

“VALORIZATION OF WASTE”

“Transformation of waste to energy, fuels, and other useful materials”

Valorization of Waste

Examples;

1. Tyres
2. Plastics
3. Composite waste

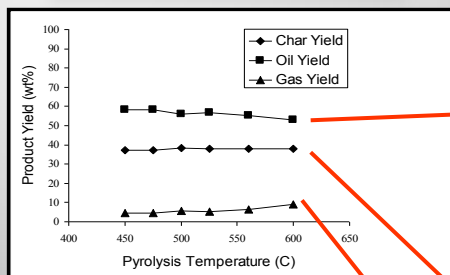
1. Waste Tyres



World
13.5 Million Tonnes/year
(1000 Million Tyres/year)

Europe
2.7 Million Tonnes/year
(200 Million Tyres/year)

Pyrolysis of Tyres



Fuel Test	Tyre Oil	Gas Oil	Light Fuel Oil
CV MJ/kg	42.1	46.0	44.8
Viscosity 60 °C	2.38	1.3	4.3
40 °C	6.30	3.3	21.0
Initial B.Pt.	100	180	200
10% B.Pt.	140	-	-
50% B.Pt.	264	300	347
90% B.Pt.	355	-	-
Hydrogen %	9.4	12.6	12.4
Carbon %	88.0	87.1	85.5
Sulphur %	1.45	0.2	1.4
Nitrogen %	0.45	0.05	0.15
Carbon residue	2.2	0.35	-
Flash point °C	20	75	79

Gas composition (wt%)

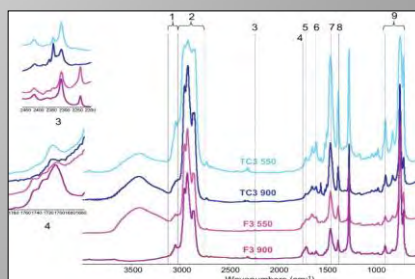
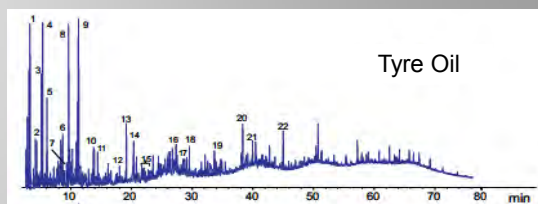
Hydrogen	0.25
Carbon monoxide	0.22
Carbon dioxide	0.60
Methane	0.96
Ethane	0.51
Ethene	0.40
Propane	0.43
Propene	0.60
Butadiene	2.13
Other C ₄ hydrocarbons	0.37
Total	4.27

Typical char properties

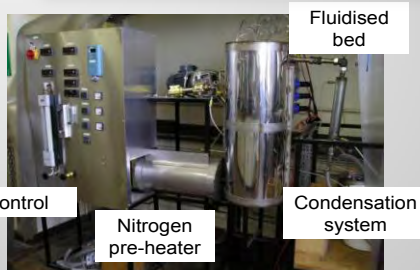
Char Test	Tyre Char
CV MJ/kg	30.5
Moisture content %	0.4
Volatiles %	2.8
Ash content %	11.9
Carbon %	94.6
Hydrogen %	1.1
Nitrogen %	0.7
Sulphur %	2.4
Surface area m ² /g	67

Tyre oil composition

Peak	Compound
1.	Cyclopentanone
2.	Dimethylcyclopentanone
3.	Ethylbenzene
4.	Xylene
5.	Styrene
6.	Ethylmethylbenzene
7.	Methylstyrene
8.	Benzonitrile
9.	Limonene
10.	Terpinolene
11.	Methylbenzonitrile
12.	Benzoic acid
13.	Benzothizole
14.	Caprolactama
15.	Methylnaphthalene
16.	Dimethylnaphthalene
17.	Pentadecene
18.	Trimethylnaphthalene
19.	Heptadecene
20.	N-hexylbenzamide
21.	Hexadecanitrile
22.	Heptadecanitrile

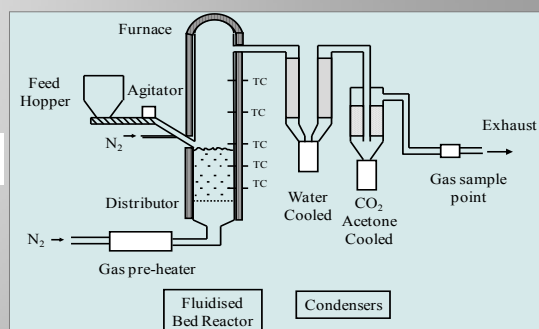


Catalytic pyrolysis of Tyres: Fuels & Chemicals



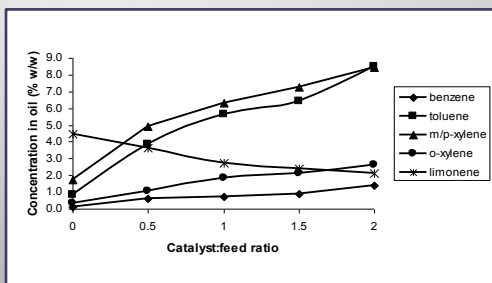
e.g. Fluidised bed catalytic pyrolysis

- Reactor – Fluidised bed
- Waste - Tyres
- Catalysts – Zeolite ZSM-5, Y Zeolite
- Temperature – 500 °C
- Bed catalyst loading 2.5 – 10 wt%

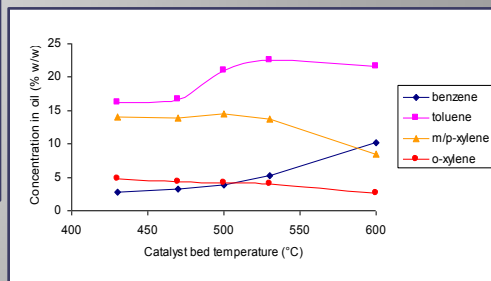


Production of premium grade fuels or chemicals;

Catalytic pyrolysis of tyres

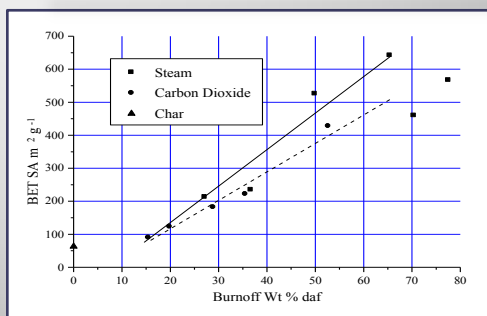


Oil Composition Zeolite ZSM-5
Fluidised bed

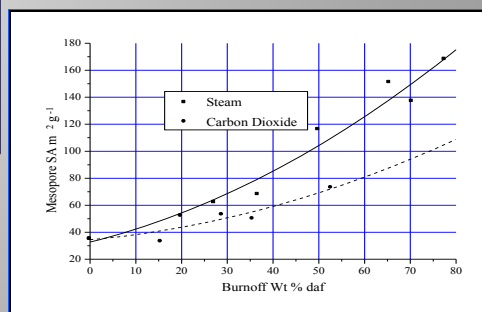


Oil Composition Y Zeolite
Fixed bed

Char: Production of activated carbons from tyres



Surface area in relation to carbon 'burn-off'



Porosity of activated carbon
in relation to carbon 'burn-off'

2. Waste plastics



World Plastics Production
245 Million Tonnes/year

Europe Plastics Production
60 Million Tonnes/year

Plastics pyrolysis: Product Yield & Gas Composition

Feedstock	Reactor Type	Temperature (°C)	Gas* (wt%)	Oil/Wax (wt%)	Char (wt%)
Plastic Mixture	Vacuum	520	6.3	91.8	1.3
Plastic mixture	Fixed bed	700 ¹	9.6	75.1	2.9
Plastic mixture	Fluidised bed	600	44.7	43.2	7.6
Plastic mixture	Fixed bed	500	85.2	12.5	3.0
MSW Plastic	Fluidised bed	787	43.6	26.4	25.4
MSW Plastic	Fixed bed	430	25		

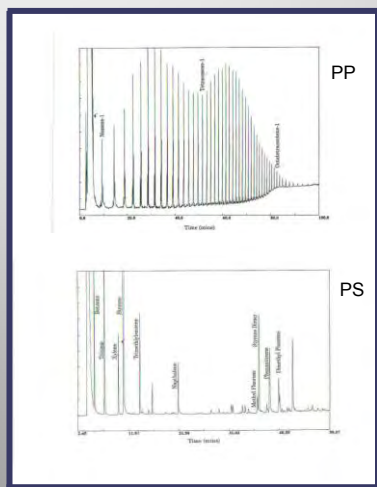
Product yield

Gas Composition

	Reactor Type	H ₂ (wt%)	CH ₄ (wt%)	C ₂ H ₆ (wt%)	C ₃ H ₈ (wt%)	C ₄ H ₁₀ (wt%)	C ₅ H ₁₂ (wt%)	C ₆ H ₁₄ (wt%)	C ₇ H ₁₆ (wt%)	CO ₂ (wt%)	CO (wt%)	HCl (wt%)
HDPE	Fixed bed	0.12	1.90	2.21	6.08	1.31	4.56	0.22	0.36	-	-	-
PE	Fluidised	0.8	23.8	6.7	20.0	0.08	5.6	-	0.6	-	-	-
LDPE	Fixed bed	0.05	1.14	1.67	4.00	1.33	4.00	0.32	2.00	-	-	-
LDPE	Ultra fast	-	22	-	28	-	18	-	-	-	-	-
LLDPE	Fluidised	-	4.6	2.2	19.4	0.8	12.0	13.1 ¹	-	-	-	-
PP	Fixed bed	0.05	0.93	1.45	3.52	1.00	3.53	0.23	1.29	-	-	-
PP	Fluidised	0.7	28.2	4.0	13.9	0.09	3.7	-	0.4	-	-	-
PS	Fixed bed	0.04	0.53	0.08	0.26	0.02	0.05	0.00	0.06	-	-	-
PS	Fluidised	-	0.06	-	0.04	-	-	-	-	-	-	-
PVC	Fixed bed	0.12	0.77	0.47	0.15	0.24	0.19	0.11	0.15	-	-	52.93
PET	Fixed bed	0.31	0.71	0.03	1.41	0.13	0.09	0.00	0.00	22.71	13.29	0.00
Polyester	Fluidised	0.3	3.8	0.2	-	0.05	0.1	-	-	26.9	17.4	-
PU	Fluidised	0.7	16.1	1.8	7.2	0.2	1.3	-	0.1	1.8	34.0	-
Mixed Plastic	Fixed bed	0.08	0.97	1.01	1.67	0.70	0.83	0.14	2.20	2.06	-	2.31
Mixed Plastic	Fluidised	0.22	2.87	2.39	5.65	1.26	5.53	0.24	6.35	-	-	1.42

Oil Analysis: Pyrolysis of plastics

Oil Composition

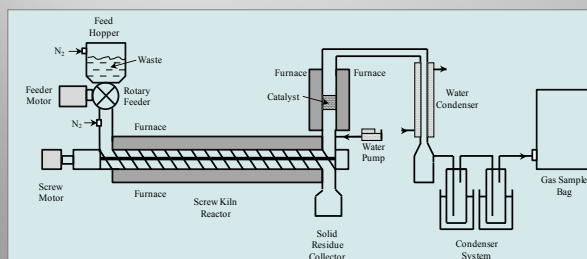
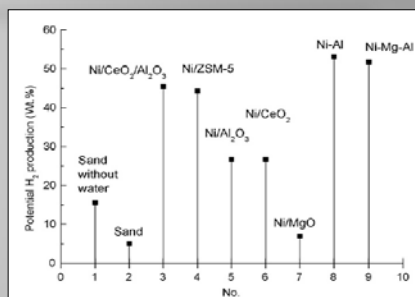
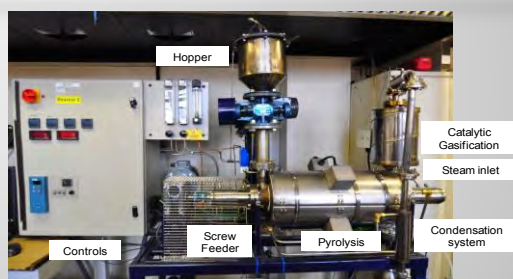


GC-FID / GC-MS

Fuel properties

Property	PE	PP	PS	Nylon	PP 50% PE 43% Nylon 7%	Polyester Styrene copolymer
Flash point (°C)	33.6	27.8	26.1	34.8	26.0	26.0
Pour point (°C)	2.7	-39	-67	-28	-5.0	-
Water content (ppm)	0.18	0.13	0.67	2500	310	-
Ash (wt%)	0.013	0.010	0.006	0.018	0.001	0.53
Viscosity (cst 50 °C)	2.19	1.9	1.4	1.8	1.485	3.9 ¹
Density (kg/m ³)	0.858	0.792	0.960	0.926	0.799	0.83
Cetane rating	-	56.8	12.6	-	54.3	-
Carbon (wt%)	-	-	-	-	-	86.1
Hydrogen (wt%)	-	-	-	-	-	7.2
Sulphur (wt%)	0.01	0.01	0.01	0.01	0.013	0.0
Initial B.Pt (°C)	-	-	-	-	-	75
10% B.Pt (°C)	-	-	-	-	-	93
50% B.Pt (°C)	-	-	-	-	-	189
90% B.Pt (°C)	-	-	-	-	-	354
CV (MJ/Kg)	52.3	53.4	50.4	44.4	46.3	33.6

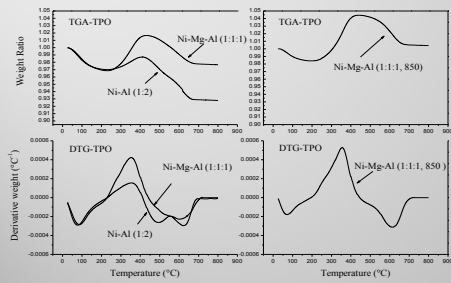
Production of hydrogen: Two-Stage Pyrolysis-Catalytic gasification



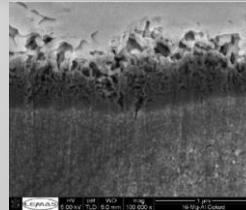
e.g. Hydrogen from Waste Plastics

- Reactor – Screw kiln
- Plastic – Polypropylene
- Pyrolysis temperature – 500 °C
- Gasification temperature – 800 °C
- Catalysts – Ni based – with steam

Coke deposition on the surface of catalyst

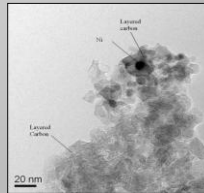


TGA-TPO and DTG-TPO of the reacted catalysts

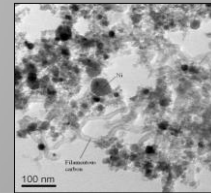


← Carbons

← Catalyst



**Layered type
carbon deposits**

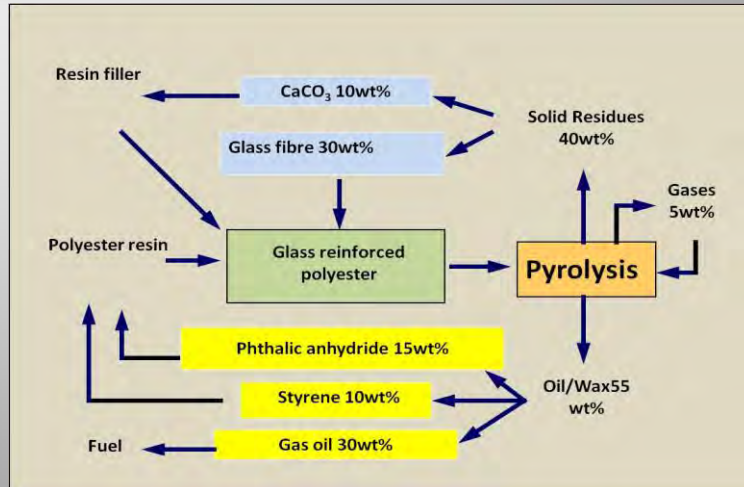


**Filamentous
carbon deposits**

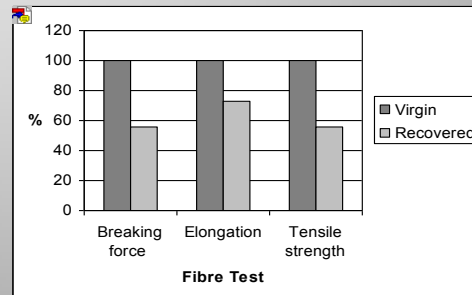
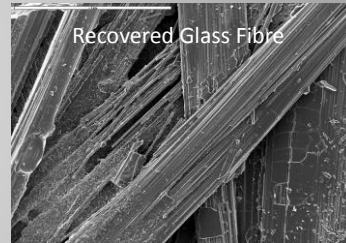
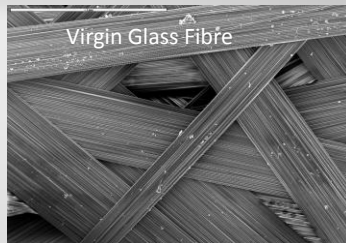
3. Composite plastic waste



Recycling process for glass fibre reinforced composite plastic waste

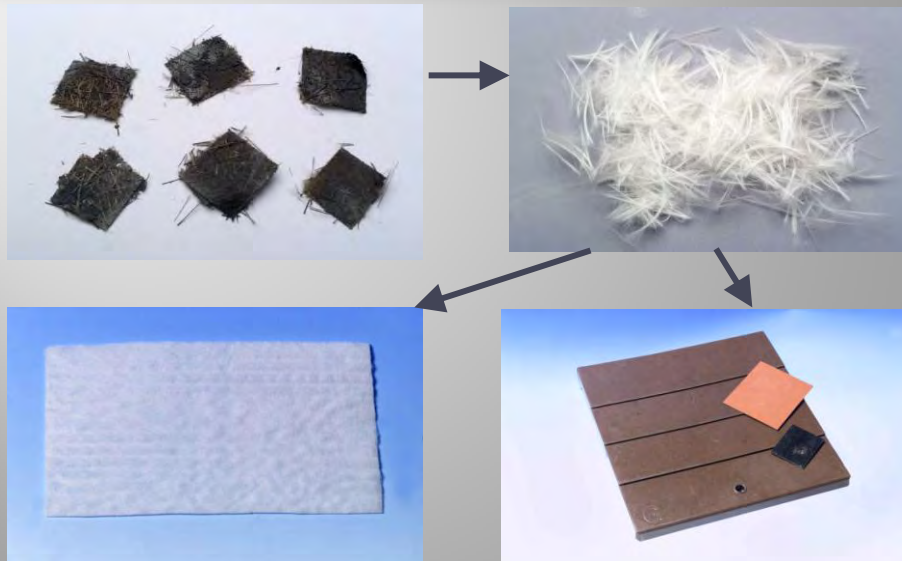


Recovered Glass Fibre



Recovered Glass Fibre: Strength Tests

Recovery and re-use of glass fibre



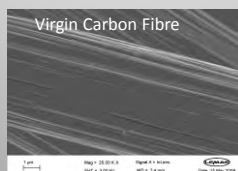
Carbon Fibre/Plastic Composite Waste



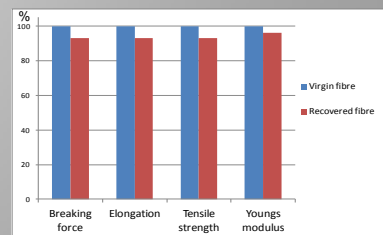
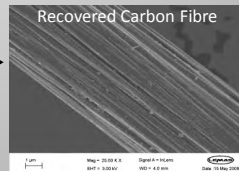
(a) Carbon fibre/ resin waste

(b) Solid pyrolysis residue

(c) Recovered carbon fibres

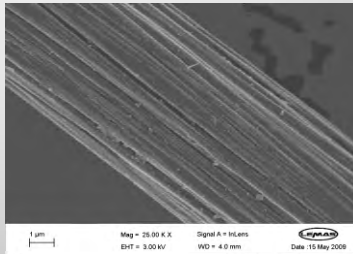


Scanning electron microscopy

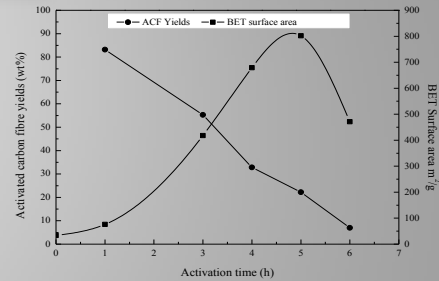
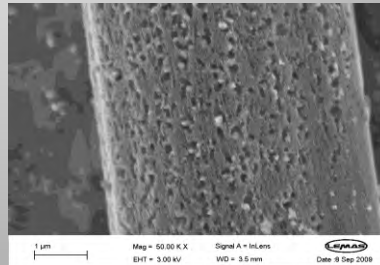


Recovered Carbon Fibre: Strength Tests

Activated Carbon Fibre



**Steam activation
of recovered
carbon fibre**



Conclusions

- ☐ Enormous research and interest in pyrolysis & gasification of biomass & waste
- ☐ Commercialization of some processes
- ☐ Upgrading is needed for biomass pyrolysis oils
- ☐ Tar reduction is a key problem for gasification
- ☐ Increasing interest in higher value products from waste

Energy, Waste & Resources – three sides of the same coin ?

The Royal Society of Chemistry : Environmental Chemistry Group

Fuels, chemicals and materials from waste

Professor Paul T. Williams

**Energy Research Institute
University of Leeds**



UNIVERSITY OF LEEDS
