Biomass fast pyrolysis: commercial uses of products in the UK context: focus on liquids upgrading and transport fuels

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Scope of presentation

- Pyrolysis: what can it do?
- Products and properties
- Commercial product options: UK context
  - Char
  - Liquids
  - Syngas
- Liquids upgrading: issues and options
- Costs of pyrolysis liquids upgrading and competition
- Conclusions

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C.A.R.E. Ltd. background

C.A.R.E. Ltd. was formed in 1996 to provide specialist technical services in bio-energy and waste to energy projects for heat, power, CHP and renewable derived products. We are:

- Specialists in thermochemical conversion – gasification, pyrolysis and combustion/co-firing,
- Practically orientated company: delivering technology designs for commercial products in gasification and pyrolysis,
- Specialists in techno-economic assessment of bio-energy technologies,
- Involved in technology development, demonstration and commercialisation in the UK, Australia, Canada and USA,
- One of a handful of independent companies with extensive practical technology experience in pyrolysis and gasification,

~80% of work is for thermochemical conversion companies, i.e., the bio-energy and waste-to-energy industry.

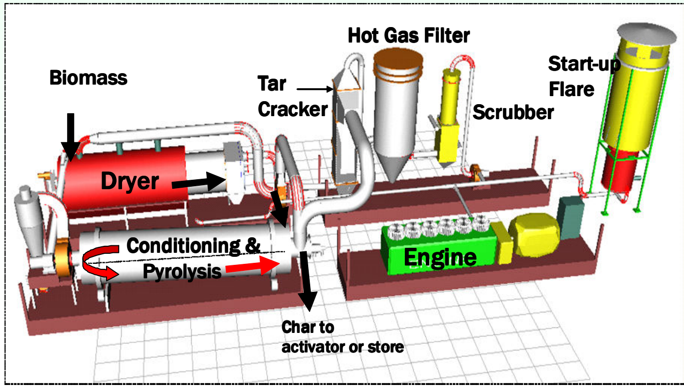
~10% for the public sector, i.e., government departments or expert evaluation work.

~10% is for universities, research institutes.

CARE Ltd. Pyrolysis examples

BEST Energies, Australia
300 kg/h slow pyrolysis [2005-2008]

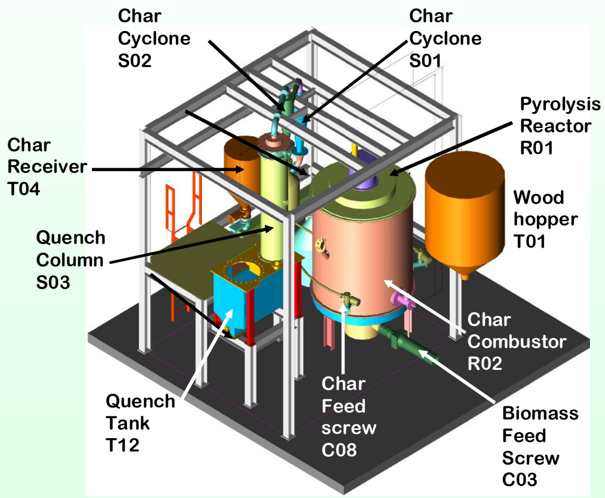
BEST Energies, USA & Australia
2, 4 t/h slow pyrolysis [2007]



Wellman Process Eng. Ltd. Fast Pyrolysis 250 kg/h [1998-2002]

Biomass Eng. Ltd. Fast Pyrolysis

300 kg/h + power generation [2005- present]



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Why pyrolysis?

- Pyrolysis may be defined as the thermal degradation of a material in the complete absence of oxygen.
- Advantages:
  - Liquids production decoupled from power generation [unlike combustion and gasification]
  - Can optimise a solid [char or chacoal], liquid [bio-oil] or gas [syngas]
  - Use for fuels, chemicals and products: bio-refinery integration and waste management
  - Very low environmental impact – low CO_2 emissions
  - High efficiency to electricity even at small scale [< 5MWe]
  - Fuel flexible systems

Pyrolysis: Advantages and Disadvantages

Advantages

- Well established technology (slow pyrolysis)
- No dioxins formation
- No thermal NOx formation
- Limited acid gas formation [H_2SO_4, HCl]
- Controlled temperature of reaction
- Modular systems possible [flexibility & availability]
- Good energy conversion efficiency
- Environmentally compliant

Dis-advantages

- Limited commercial experience/track record of some companies in the UK
- Gas cleaning for engines and/or turbines may be expensive [subject to feedstock]
- High cost for waste disposal v's landfill

Thermal Conversion Products

	Char*	Liquid*	Gas*
SLOW PYROLYSIS Low-moderate temperature (< 400℃) Very low heating rates (<10K/min) Long solid and gases residence times	35%	30% (70% water)	35%
FAST PYROLYSIS FOR LIQUIDS Moderate temperature (~450-550℃) High heating rates (>100K/s) Short vapour residence time (<2-3 s)	12%	75% (25% water content)	13%
FAST PYROLYSIS FOR GAS High temperature (>800℃) High heating rates (>100K/s) Variable vapour residence time (>2 s)	6%	10wt%	84wt%
GASIFICATION high temperature (>800℃)	5%	5% (tar) (80% water)	90%

* Indicative values – very dependent on feedstock and process parameters used – 13 main process parameters

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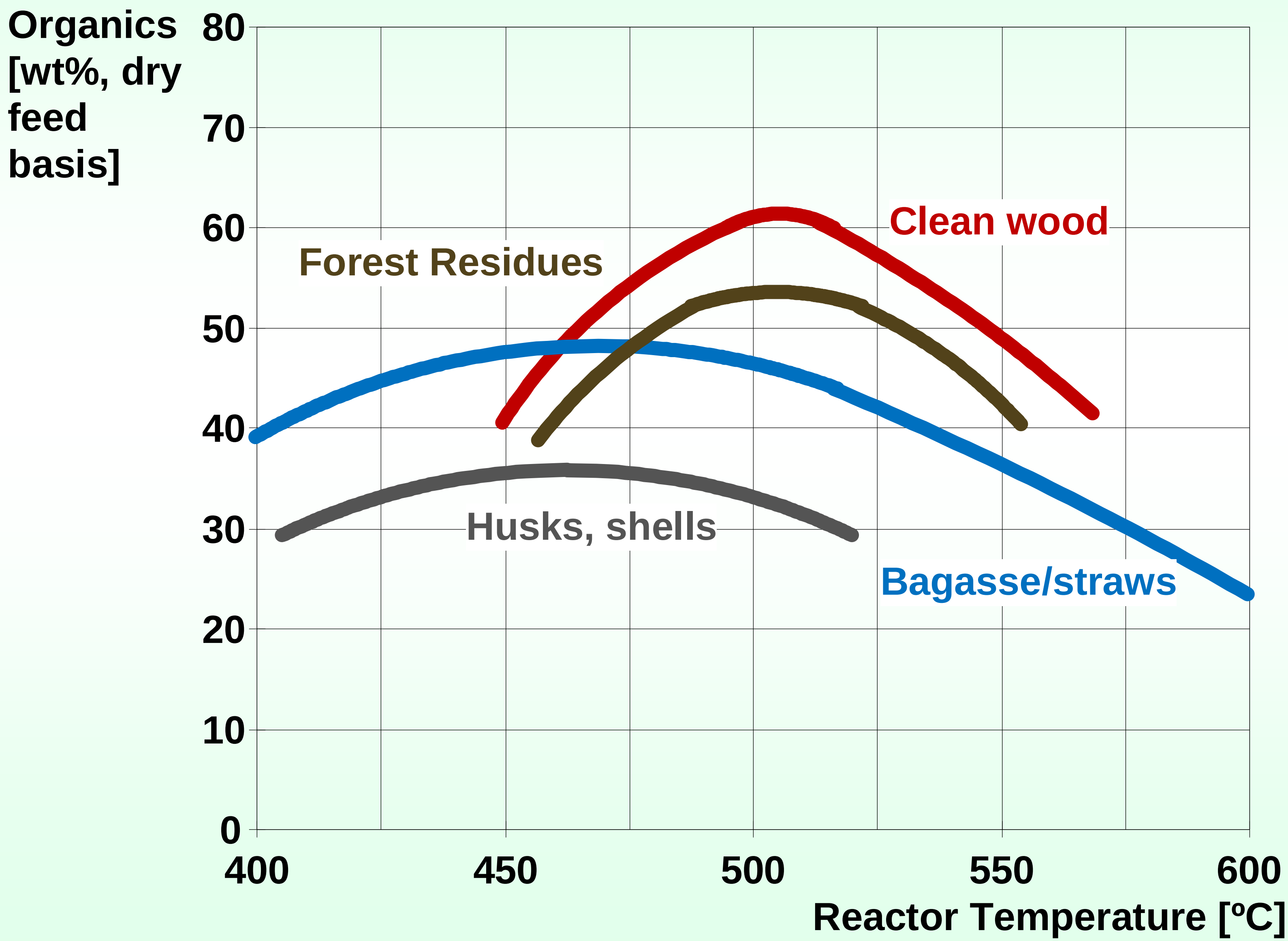
Fast Pyrolysis Organics Yields [wt%, dry biomass]



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UK Pyrolysis plants: selection

- PurePower, Huntingdon: 4 MWe [unknown]
- EPI, Mitcham: 1 t/h, 350 kWe [operational]
- University of Aberystwyth, Aberystwyth : 500 kg/d output biochar unit [operational]
- Hudol, Cardiff: 1.5 t/h demo/R&D unit [available]
- NewEarth, Canforth: 1 MWe [operational]
- First London Power, London: 0.5 t/h [demonstrator]
- GEM, Scarborough, 1.5 t/h input, 1 MWe output [dormant]
- Biomass Engineering Ltd., Newton-le-Willows: 250 kg/h fluid bed fast pyrolysis for liquids unit [not built yet]
- KwikPower/Wellman Process Engineering Ltd., Oldbury 250 kg/h fluid bed fast pyrolysis for liquids – [dormant]

- Others including Plasmera, Waste2Tricity, PowerHouse Energy, 2G BioPower Ltd. (Envergent technology representative)

- Many R&D units available in universities;
- Small-scale systems; regional charcoal producers

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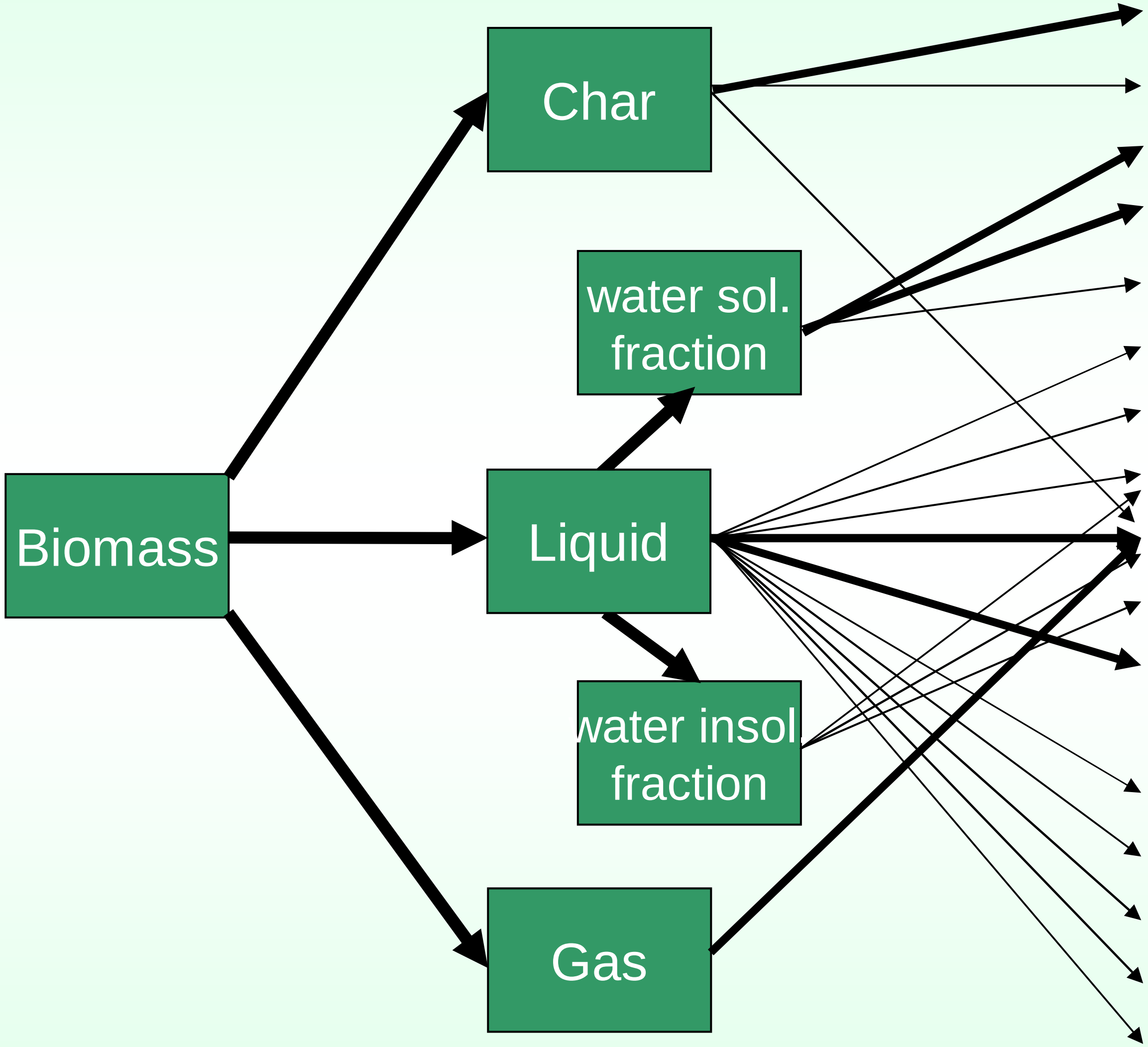
Bio-refinery – Pyrolysis I



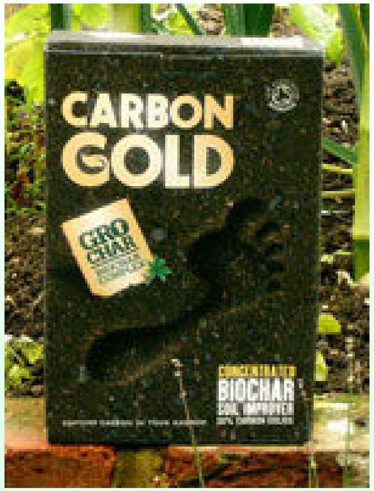
	STATUS
Activated carbon	C
Carbon black (from rubber)	D
Meat browning agent	C
Smoke flavors, methanol	C
Acids / acetates (road deicers)	C
Biolime™	D
Slow-release fertiliser	R&D
Wood preservatives	D
Boiler/engine/gasifier fuel	C
Adhesives	D
Hydroxyacetaldehyde (glycolaldehyde)	C
Levoglucosan	D/C
Phenols (from lignin)	C
Furfural (from xylose)	D
Levulinic acid (from glucose)	R&D
Transport fuel	R&D

Key: C: Commercial Product
D: Demonstration
R&D: Research and Development

 Prins, W., BTG, the Netherlands, 2006

Char: Commercial Biochar UK

- Identified 2 specific commercial producers of biochar in UK [exc. standard charcoal retailers]
- Wide price ranges from £100/t to over £16,000/t, depending on quantities and geographical location
- Some small "cottage industry" producers
- UK Commercial biochar examples:
  - Black Gold – Nutrichar: £4.99 for 300g
  - Carbon Gold – Grochar: £9.95 for 1.4 kg



Char and Syngas Analysis

Char yield between 27 and 50% of feed (dry)

Activation to give high surface areas – up to 800 m^2/g

Sampling possible directly from kiln or char activator

50% Carbon from sequestration biomass remains in char – potential

Gas analysis with Greenwaste feed

Gas CV approximately 7 MJ/kg

Gasifier gas approximately 3-4 MJ/kg depending on feed

Clean gas suitable for use in engines or boilers

"Tar" < 250 mg/m^3

Renewable source of energy

		Conc. (Vol%)
Carbon Monoxide	CO	22.5
Hydrogen	H2	15
Methane	CH4	7.9
Ethane	C2H6	0.1
Propane	C3H8	0
Ethylene	C2H4	0.8
Acetylene	C2H2	0.3
Carbon Dioxide	CO2	13.4
Nitrogen	N2	40

Greenwaste Char Analysis

	%
Ash	16.3
Carbon	75.3
Hydrogen	1.88
Nitrogen	0.35
Sulphur	0.03
Oxygen	6.2

Chicken Litter Char

BEST Energies, Australia

Integrated slow pyrolysis process

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Why convert nice, harmless biomass to this nasty, corrosive liquid?

- Wood/waste biomass is not economically transportable over long distances [~ 40-50 mile limit in the UK] for energy production. Costs ~£10/t/50 miles to move wood.
- Liquid has other high value non-energy, high value applications and uses [resins, fertilisers, smoke flavourings, speciality sugars, etc.].
- Energy density of ~2½-5 times that of the starting biomass.
- Liquids can be used as an energy intermediate in production of liquid transport fuels [upgrade, gasify liquids or FT synthesis from syngas].
- Power generation decoupled from liquids production – can be stored and used as required. Can't easily be done with combustion or gasification.
- Low CO_2 impact of ~50 g CO_2/kWh compared to 1100 g CO_2/kWh for coal on a life cycle assessment basis for power applications.

Fast pyrolysis for liquids

- Biomass is heated as quickly as possible [few seconds- use small particles]
- To a carefully controlled temperature (~450-500°C, depending on the feedstock)
- Products are cooled as quickly as possible (<2 s)
- The liquid has unique ''properties''
  - Dark brown mobile liquid,
  - 100+ chemicals (70% identifiable),
  - Combustible, but not flammable,
  - Heating value ~ 14-16 MJ/kg wet,
  - Not miscible with hydrocarbons,
  - Density ~ 1.2 kg/l,
  - Acid, pH ~ 2-3,
  - Pungent odour,
  - High chemical instability - reacts slowly with air

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Pyrolysis Liquids Commercial Uses

- Comprise 65%+ of the products in mass and energy terms
- Liquids multiple uses:
  - Chemicals [acetic acid, hydroxyacetaldehyde, levoglucosan, glycolaldehyde],
  - Products synthesis: slow release fertilisers, resins, preservatives, soil additive [lignin fraction],
  - Heating oil [Metso, Finland]
  - Liquids upgradable to hydrocarbons.

  - Very limited experience in liquids combustion for power in the UK
  - Preferable to use all of the liquid in an application

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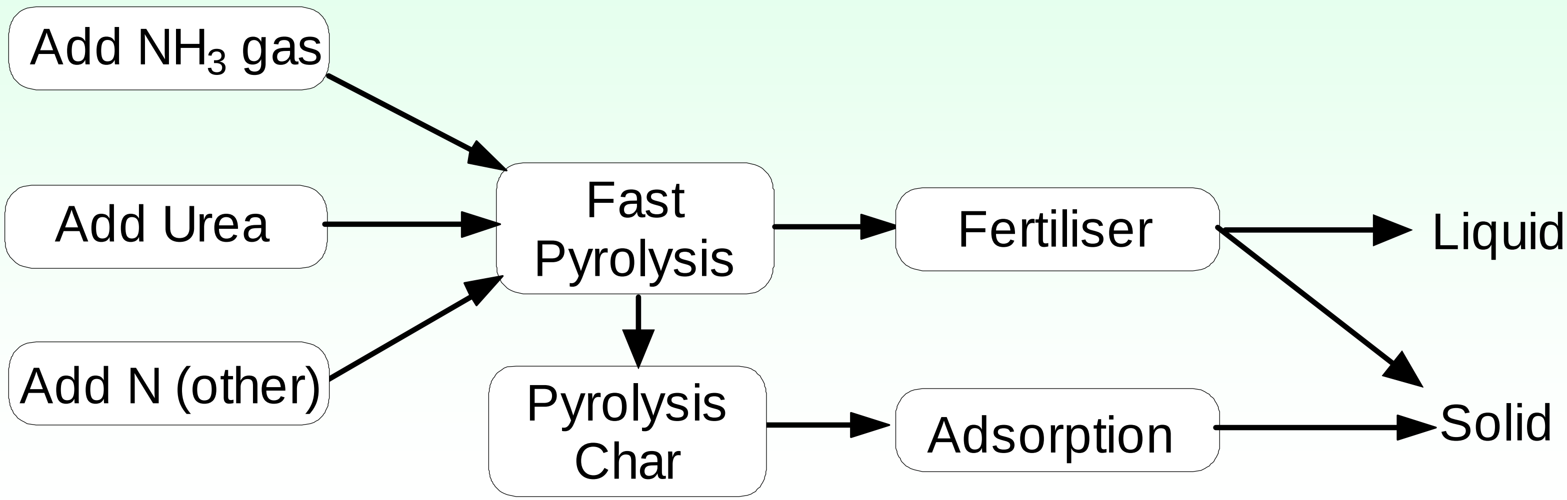
Slow release fertilisers by fast pyrolysis



- Comparable growth rates to Multicote and Osmocote on pot trials
- On grass, lower N leachate rates with fast pyrolysis N fertiliser observed compared to standard N fertilisers [200 kg N/ha]
- N production cost of €2000/t [2002] at output of 10,000t/y

EU project, FAIR6-CT98-4042, 1998-2002

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Ormrod Diesels: UK Power generation

- Ormrod developed and tested a dual fuel diesel engine for use with pyrolysis liquids.
- 250 kWe ERDFS6, 6 cylinder, 700 rpm.
- 3 cylinders modified for pilot diesel injection at 5% energy.
- Computer controlled start-up and shut-down.
- 500 hours operation.
- Lower NOx, higher CO in exhaust.
- 31-32% efficiency to electricity with pilot diesel.

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Future Blends

Future Blends' mission to develop pyrolysis-based technology for the cost-competitive production of low carbon transport fuels from waste biomass. This includes upgrading of pyrolysis oil for use in transport fuels or as a refinery feedstock for the manufacture of transport fuels. For this to be possible, the upgrading process needs to substantially reduce the acidity, water and oxygen content of the oil, and improve its stability.

Current status is:

- Ongoing completion of new facilities in Milton Park, Oxford
- Operation of a 0.5 kg/h fluidised bed reactor system
- Design and build of a 5 kg/h fluidised bed reactor system
- Strategies for upgrading the pyrolysis products to a mix of green chemicals, refinery feedstock and hydrocarbons > C_6
- Supported by and working with Conversion And Resource Evaluation Ltd. and Catal International Ltd.

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Syngas: comparison of analyses

Process	Pyrolysis UK	Pyrolysis UK	Pyrolysis Germany	Thermolysis France	Pyrolysis UK		Downdraft Gasification UK
Feedstock	Chicken litter	Wood	MSW	MSW	Sewage sludge		Mixed conifer
CO	14.58	30.5	14	19.1	20		21.24
CO_2	10.80	15.0	7	28.8	14		11.82
H_2	24.23	24.6	15	12.7	23		15.38
CH_4	34.44	21.8	1	16.0	17		2.05
C_2H_4	8.42	5.6		5.50	8		0.48
C_2H_6	0.70	0.7		4.9	4		0.03
C_3H_6				13.0	4		0.01
C_3H_8	0.65	0.4					0.00
C_4+C_5	2.00				5		0.0
N_2	3.70	0.9	62	0			49.0
LHV [MJ/Nm^3]	26.57	17.5	4	25.1	24.8		5.0

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Syngas commercial use

Syngas use:

- Cleaned up and burnt for power in a gas engine or turbine [2ROCS @ £40/ROC + base price of £60/MWh= ~£140/MWh],
- H_2 source if shifted and demethanated [GTI approach]
- Used after catalytic shift for FT synthesis to diesel equivalent. Only relevant to very high T pyrolysis:

  $CO_2 + H_2 \rightarrow CO + H_2O$ (Reverse Water-Gas Shift)

  $nCO + 3nH_2 \rightarrow nCH_4 + nH_2O$ (Methanation)

  $nCO + (2n+1)H_2 \rightarrow C_nH_{2n+2} + nH_2O$ (Paraffins)

  $nCO + 2nH_2 \rightarrow C_nH_{2n} + nH_2O$ (Olefins)

Process use

- For heating the pyrolysis process,
- Fluidise reactor
- Burnt for process heat and/or drying.

Analysis of Fast Pyrolysis Liquids

Organization	Feedstock	Water content (%)	Elemental analysis[a]				Higher heating value (MJ/kg)
			C (%)	H (%)	N (%)	O (%)[b]	
Federal Research Center for Forestry and Forest Products, Institute for Wood Chemistry (IWC), DE	Beech	31.9	54.35	6.80	0.22	38.63	21.2
ENSYN Technologies Inc. (ENSYN), CA	Mixed Hardwood	26.4	59.89	5.98	0.34	33.79	22.8
Union Electrica FENOSA (FENOSA) I, ES	Eucalyptus	25.6	54.44	6.10	0.39	39.07	20.2
Union Electrica FENOSA (FENOSA) II, ES	Wheat/Straw	36.0	53.53	6.42	0.64	39.41	20.3
Aston University (ASTON), UK	Poplar	16.1	53.55	6.50	0.35	39.60	20.3
National Renewable Energy Laboratory (NREL)[c],US	Poplar	16.3	56.20	6.64	0.30	36.86	21.9
Twente University (BTG), NL	Mixed Softwood	18.6	54.84	6.51	0.39	38.26	21.0
Technical Research Center of Finland (VTT), FI	Pine	17.4	55.23	6.60	0.11	38.06	21.3

A **Based on water free oil.**

B **Calculated by difference.**

C **Hot filtered oil.**

B Scholze, D Meier, "Characterization of the water-insoluble fraction from pyrolysis oil (pyrolytic lignin)". Part I. PY–GC/MS, FTIR, and functional groups", Journal of Analytical and Applied Pyrolysis, Volume 60, Issue 1, June 2001, Pages 41–54

Upgrade options for liquids

- Hydrodeoxygenation (HDO):

  $CH_{1.33}O_{0.43} + 0.77\ H_2 \rightarrow CH_2 + 0.43\ H_2O$
- Catalytic (Zeolite) Cracking:

  $CH_{1.33}O_{0.43} + 0.26\ O_2 \rightarrow 0.65\ CH_{1.2} + 0.34\ CO_2 + 0.27\ H_2O$
- Reaction with alcohols (esterfication):

  $R_1\text{-COOH} + R_2\text{-OH} \leftrightarrow R_1\text{-COO-}R_2 + H_2O$
- Decarbonylation

  $CH_{1.33}O_{0.43} \rightarrow 0.78\ CH_2 + 0.22\ CO_2$

- No single approach is sufficient to fully utilise the liquids – multiple processing steps needed
- Zeolites ideally suited to reactants with EHI> 1.3-1.6 to avoid coking and promote H/Cs: pyrolysis organics EHI is <0.2 $\rightarrow$ C and H_2O formation.

The EHI is defined as: $(H/C)_{effective} = (H-2O-3N-2S)/C$

where: H, C, O, N and S are atoms per unit weight of sample of hydrogen, carbon, oxygen, nitrogen and sulphur respectively.

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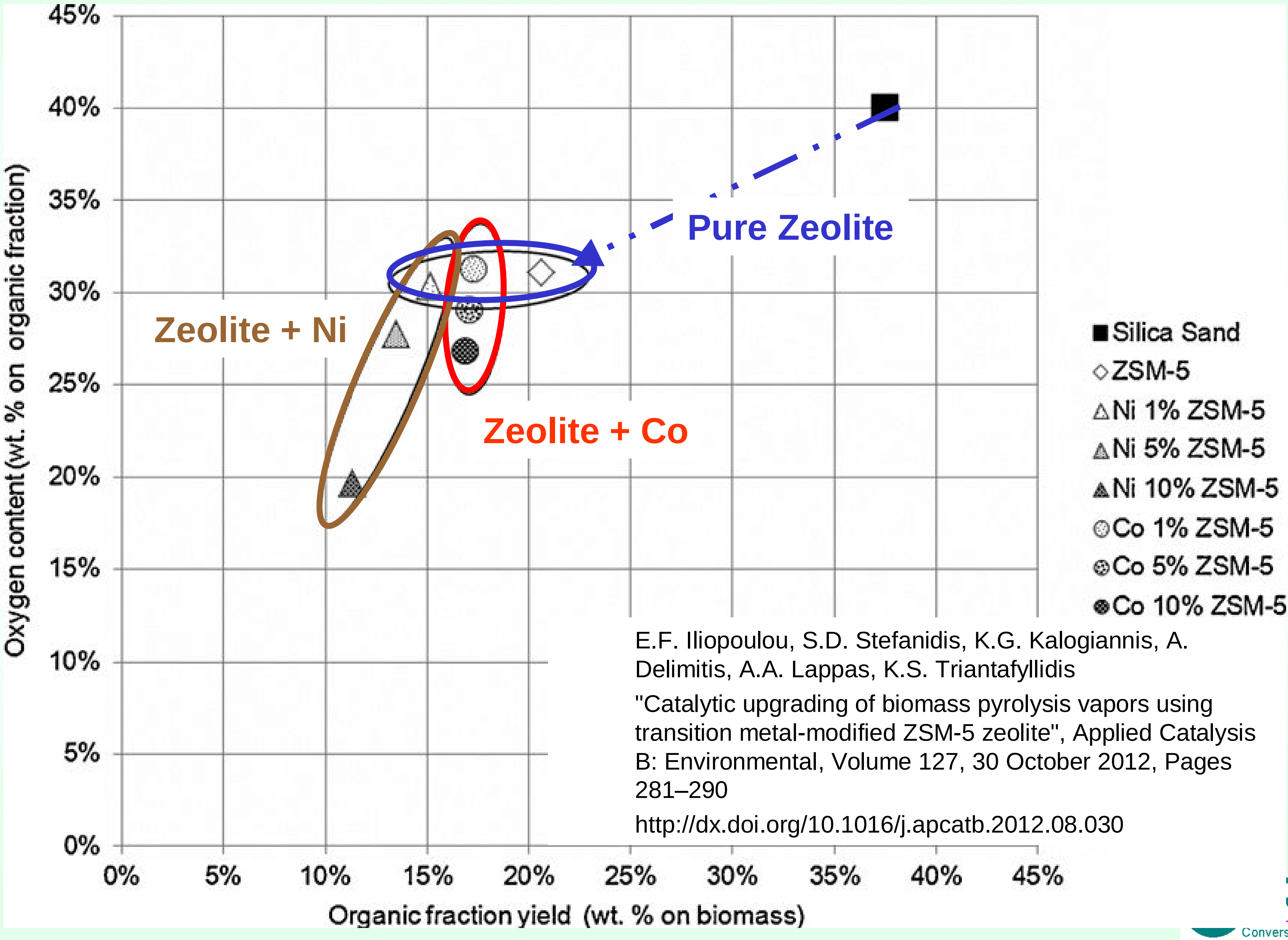
Zeolite Cracking of Pyrolysis Vapours

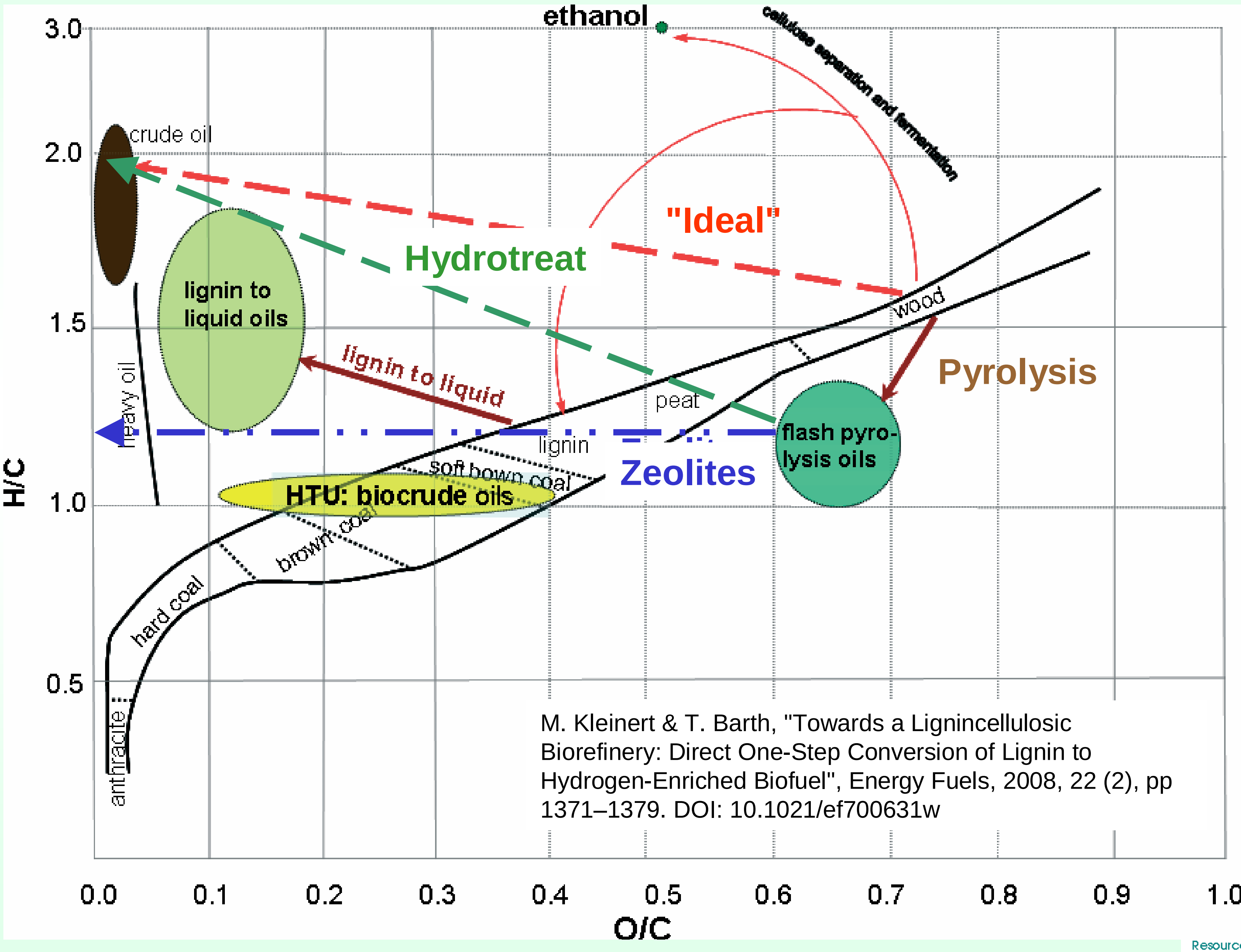


E.F. Iliopoulou, S.D. Stefanidis, K.G. Kalogiannis, A. Delimitis, A.A. Lappas, K.S. Triantafyllidis

"Catalytic upgrading of biomass pyrolysis vapors using transition metal-modified ZSM-5 zeolite", Applied Catalysis B: Environmental, Volume 127, 30 October 2012, Pages 281–290

http://dx.doi.org/10.1016/j.apcatb.2012.08.030

Where do we need to get to?



M. Kleinert & T. Barth, "Towards a Lignincellulosic Biorefinery: Direct One-Step Conversion of Lignin to Hydrogen-Enriched Biofuel", Energy Fuels, 2008, 22 (2), pp 1371–1379. DOI: 10.1021/ef700631w

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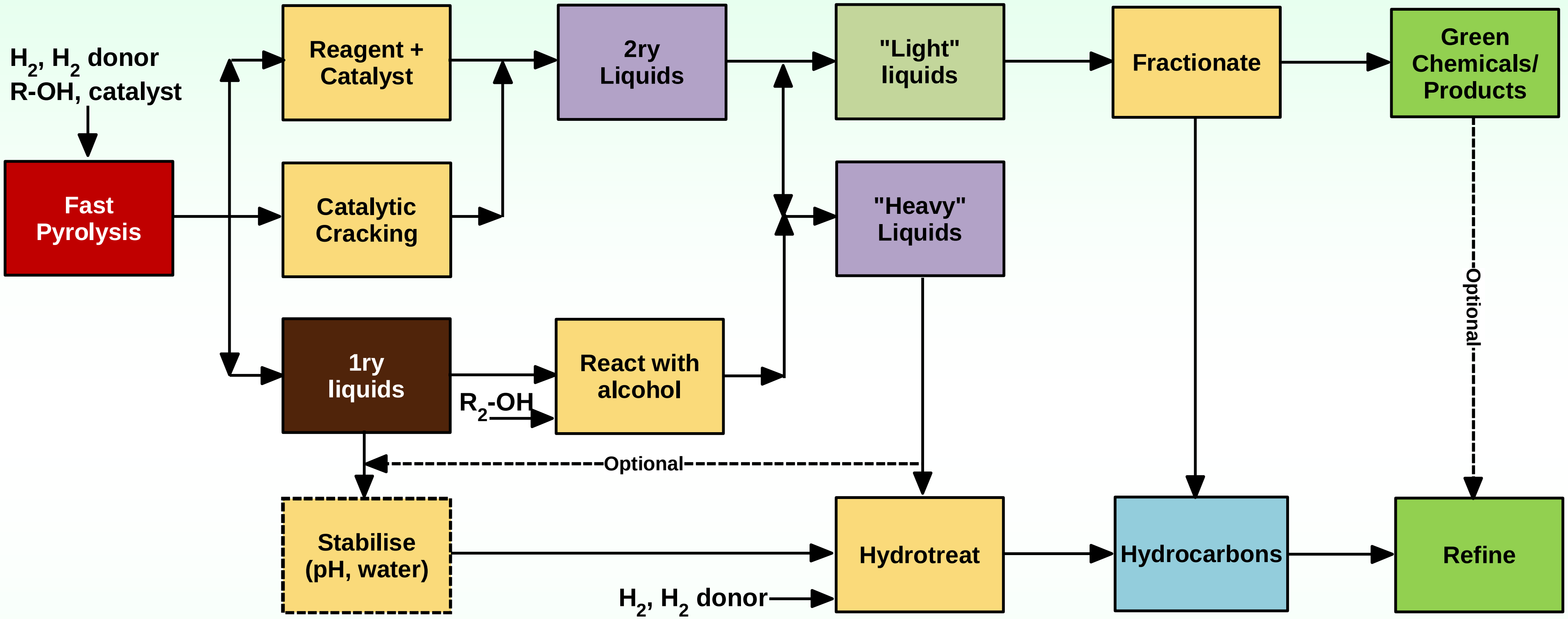
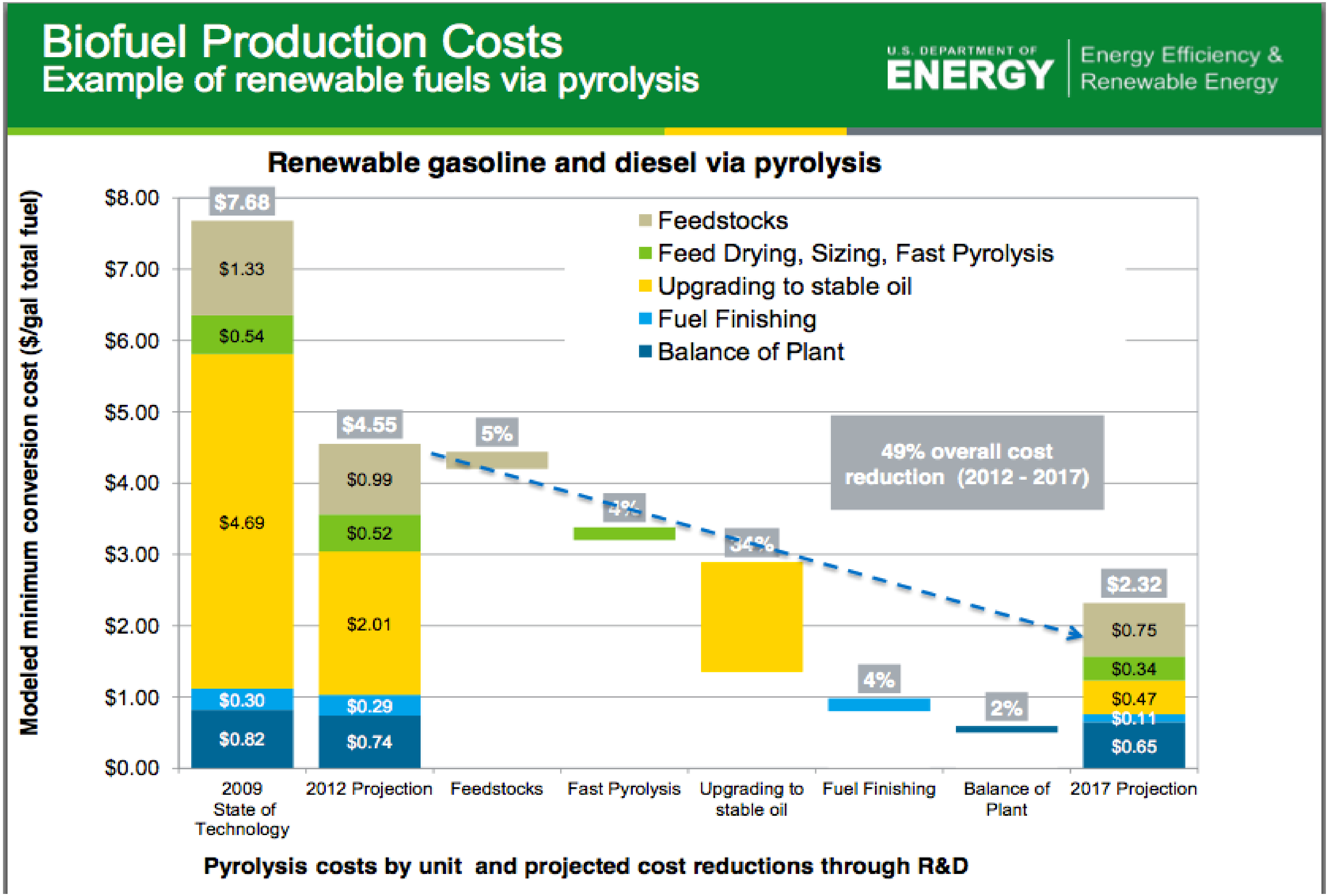
Pyrolysis Liquids Upgrading Options



- Range of processing options with their own advantages and disadvantages, but diminishing C retention in final product – and yield.
- H_2 addition will be needed in the process [unless you accept low H/C yields, high C loss and water]



Z. Haq, "Biofuels Design Cases", US DoE, April 2012
http://www.usbiomassboard.gov/pdfs/tac_design_case_haq.pdf

Costs of Transport Fuels I

Process	**Biomass throughput**	**Fuel output**	**Capital investment**	**Biomass cost**	**Fuel production cost**	**Assumptions**	Ref
Centralised gasification and Fischer–Tropsch synthesis	144,673,913 GJ/y (7,419,175 dry tpy)	66,550,000 GJ/y (550 million gal gasoline eq/y)	$1.63 billion	$40/ton	$12.89/GJ ($1.56/gge)	$US\$_{2008}$ Biomass HHV=19.5 MJ/kg Biomass to fuel efficiency=46%	1
Distributed fast pyrolysis, pyrolysis liquids gasification and FT synthesis	30,250 dry tpd (8,833,000 dry tpy)	66,550,000 GJ/y (550 million gal gasoline eq/y)	$4.1 billion	$40/ton	$13.22/GJ ($1.60/gge)	$US\$_{2008}$ Biomass HHV=19.5 MJ/kg Biomass to pyrolysis liquids eff. = 69% Pyrolysis liquids to fuel efficiency=56% Charcoal credit=$50/ton	1
Pressurised gasification and FT synthesis (IGT–R)	80 dry tph (640,000 dry tpy) 400 MWth	164 MWth	$341 million	$2/GJ $23.1/ton wet	$14/GJ	$US\$_{2001}$ Biomass LHV= 11.55 GJ/tonne 30% moisture Overall energy efficiency = 41%	2
Gasification of pyrolysis liquids & biochar slurry and FT synthesis	80 dry tph (640,000 dry tpy) 400 MWth	164 MWth	€500 million	€60/t €4.8/GJ Plus €9/t loading, €0.0475/t/km	€1.39/l €50–60/GJ	$€_{2010}$ 25 years ROI Discounting factor 8% Energy efficiency 41% Plant availability 8000 h/y	3

Costs of Transport Fuels II

Process	Biomass throughput	Fuel output	Capital investment	Biomass cost	Fuel production cost	Assumptions	Ref
BtL FICFB Carbo–V H–DWS S–DWS H–bioliq S–bioliq	40 dry tph (280,320 dry tpy) 200 MWth	NK	NK	€70/t, 50% moisture	€ 87.92 /GJ € 49.69 /GJ € 62.00 /GJ € 60.36 /GJ € 62.83 /GJ € 53.22 /GJ	Projection $€_{2015}$ Plant availability 80% Plant life 20 years Overall efficiency 28 to 50%	4
Fast pyrolysis, hydrotreating and hydrocracking	2000 dry metric tpd (657,000 tpy)	76 million gal/y	$303 million	$50.7/ dry metric tonne	$2.04/gal $1.34/gallon EtOH eq. ($16.05/GJ)	$US\$_{2007}$ n^{th} plant ROI=10% Plant life=20 years EtOH LHV= 27.6 MJ/kg EtOH density = 0.79 kg/litre	5
UOP	NK	NK	NK	$35/ton	$2.01/gal $1.27/gal EtOH eq. ($16.1/GJ)	$US\$_{2005}$ ROI= 10% Purchased hydrogen $25/bbl pyrolysis oil cost	6
KiOR	1500 dry tpd (500,000 tpy)	100,500 gal/y	NK	$72.3/ dry t	$550/ metric tonne $0.50/litre $1.10/gal EtOH eq. ($13.3/GJ)	$US\ \$_{2010}$ Yield= 67 gallons per dry tonne Costs of financing and facility depreciation are excluded	6

Petrol[1] £39.0/GJ (excluding tax 13.7): Diesel[1] £36.2/GJ (excluding tax 13.5): Bio–diesel/RME[2] £23.7/GJ
Bio–ethanol[2] £23.2/GJ Heavy fuel oil[1] £11.4/GJ
Notes: 1 UK selling price 13.06.2011, Energy Price Statistics DECC; 2 EnAgri Newsletter, June 2011 – European wholesale prices

Cost references for slides 27 and 28

1. M. M. Wright, R. C. Brown, A. A. Boateng, Modeling and Analysis: Distributed processing of biomass to pyrolysis liquids for subsequent production of Fischer-Tropsch liquids, *Biofuels, Bioprod. Bioref*. 2:229–238 (2008); DOI: 10.1002/bbb
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3. G. Biossonnet et al., BTL Process Development: Simulation and Technoeconomic Assessment of Several Technical Options, IFC 2010 4th International Freiberg Conference on IGCC and XtL Technologies, Dresden, 3-6 May 2010
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5. Jones, S.B., et al., Production of gasoline and diesel from biomass via fast pyrolysis, hydrotreating and hydrocracking: a design case. 2009, PNNL.
6. Conversion And Resource Evaluation Ltd. internal assessment based on published data (2011).

Conclusions and Observations

- No commercial liquids production in the UK of upgraded transport fuels or refinery feedstocks.
- Very limited commercial pyrolysis applications: power generation dominant. Optimal syngas use is power generation in short term.
- Emerging biochar market: horticultural applications emerging, though limited technologies.
- Competing technologies: FT, biodiesel, bio-ethanol
- Liquids upgrading is a serious challenge: multiple processing steps needed.
- R&D at universities and SMEs – nascent industry.
- RTFO only stimulus for non-energy needs.