Recovery & re-use of carbon fibres for high performance applications

Workshop Session D – AFRA 2016

06/27/16 14:00

Agenda & Aims

An appreciation of the challenges and potential of recovered carbon fibre – Recovery and re-use technologies, commercial & R&D state of the art

- Overview – Motivation for recycling and current global status

- Fibre recovery processes overview and physical / mechanical properties of recovered fibres
- Questions & discussion

- Fibre re-use – fibre form & challenges,
- Detailed re-use avenues & markets
- Questions
- Summary & future outlook

UoN Polymer Composites Group

- UoN Polymer Composites group is one of largest groups in UK
- Group head Prof Nick Warrior
  - 11 faculty staff
  - 3 technicians
  - 15 postdoctoral researchers
  - 30-40 PhD students
- Research areas
  - Analysis of textile composites
  - Failure analysis
  - Resorbable composites
  - Automated manufacture
  - Recycling of composites

Introduction

- Prof Steve Pickering
  - Head of Department – Mechanical, Materials & Manufacturing Engineering
  - Interests;
    - Thermodynamics, fluid mechanics, heat transfer, energy efficiency
  - Active in composites recycling since ~1994

- Dr Tom Turner
  - Associate Professor – Polymer Composites group
  - Interests;
    - Re-use of recovered carbon fibres, discontinuous fibre preforming methods, composites automation
  - Active in composites recycling since ~2005

Section:01
Introduction

Why recycle? - Motivation

- Carbon fibre is valuable > $20,000 / T
- Carbon fibre production is very energy intensive – 200-600GJ/T
- Increasing global pressure on OEM’s to provide recycling routes – but still relatively little legislation governing this

- Carbon fibre based composites have potential for significant weight saving on a wide variety of structures
- Environmental business case for CFRP use on aircraft is overwhelming

Why recycle? – Environmental Issues

- Whole life cycle strategy must be employed
- Potential to recover carbon fibres at much reduced energy levels over virgin fibres (<10% ?)
- Using rCF to displace lower energy content materials may not be beneficial unless there is a benefit in reducing energy consumption during use
- If recycling CF does not save more than 30GJ/T of CF recycled it would be better to incinerate with energy recovery!

- *This governs where we seek to re-use the recovered fibres!*

Why recycle? - Scope

- Our current focus is primarily on cured thermoset epoxy/carbon fibre composite waste…

- Recycling covers manufacturing scrap and end-of-life parts
  - Dry fabric / bobbin ends
  - Trim scrap – dry fabric and pre-preg
  - Other manufacturing waste / cured trim scrap
  - End of life components – probably contaminated

- *Prioritise reuse as much as possible…*

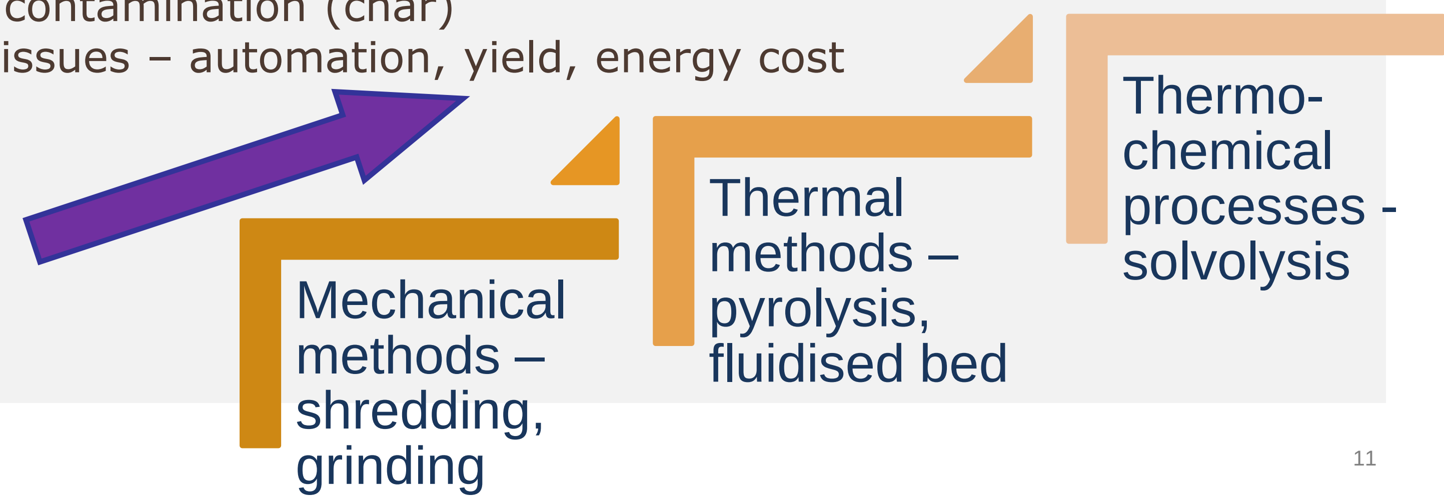
Current status of CF recycling

- Defining features of current status:
  - Increasing interest from manufacturers
  - Increasing volumes of material, both currently and predicted
  - Uncertainty over value of fibres and supply chain – *a lack of established markets*
  - Significant differences to other forms of recycling
- Current technical barriers to increased recycling
  - Difficulty in maintaining product consistency across a wide range of operating conditions and material types
  - High levels of hand labour generally – but particularly in preparation of materials prior to fibre recovery
- Current R&D efforts
  - Development of improved fibre recovery processes
  - Development of fibre re-use approaches
  - LCA

Introduction – Recycling routes

- Want to extract maximum value from the material – normally prioritising fibres
- Several processes exist for the separation / removal of matrix material…
- Processes can be distinguished by several factors
    - Fibre mechanical properties
    - Fibre length and length degradation
    - Fibre surface chemistry
    - Degree of contamination (char)
    - Hardware issues – automation, yield, energy cost

Increasing fibre value, process complexity



Commercial Operations

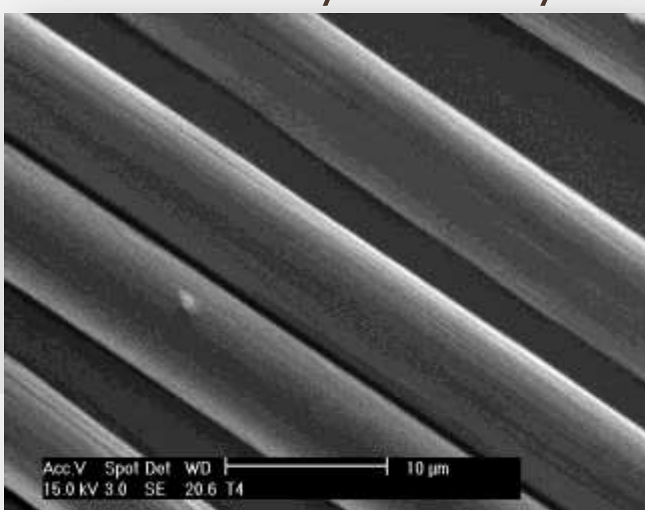
- 3 Main commercial operations with several smaller companies
- Several trade bodies also active in promoting recycling
- Pyrolysis is main process – 1000-2000 Tonnes/yr capacity
- CF part production is widely dispersed…

CarbonConversions (2000 T pa)
ELG Carbon Fibre Ltd (2000 T pa)
CFK Valley Stade Recycling (1000T pa)

Aircraft Fleet Recycling Association
Airbus Composite Recycling Advisory Board
Japan Carbon Fibre Manufacturers Association

Main R&D Centres

- Several UK & international groups investigating CF recovery & re-use
- Main areas
  - Developing new fibre recovery processes (e.g. Electrodynamic fragmentation, supercritical fluid processes)
  - Optimisation of existing processes (minimisation of char in pyrolysis)
  - Fibre re-use approaches
  - Life Cycle Analysis & energy use

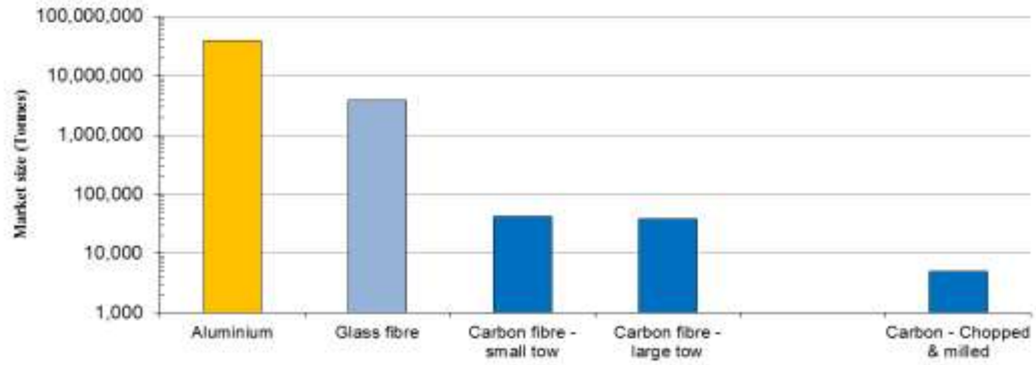


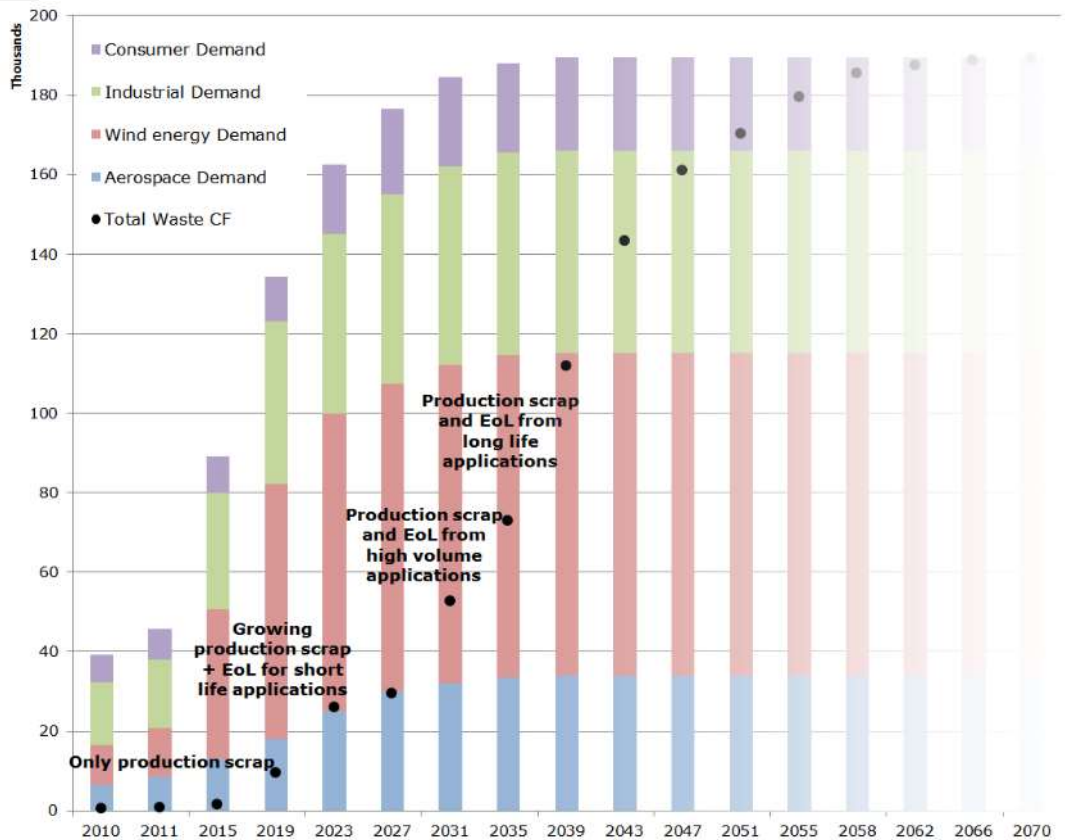
Global outlook

- Interest from manufacturers is increasing
- Legislative influences– Automotive and aircraft?
- Massive growth in CF use forecast – recycling operations must be in place
- Existing commercial ventures typically support a significant manufacturing site – questions over supply chain

Market Size

- GF market much bigger but CF potentially more valuable
- ~3000T of CF composite scrap currently generated worldwide
- Rough estimates of scrap can be generated from lifespans and ramp estimates
- **Large increases in scrap forecast over next 10,20,40 years**

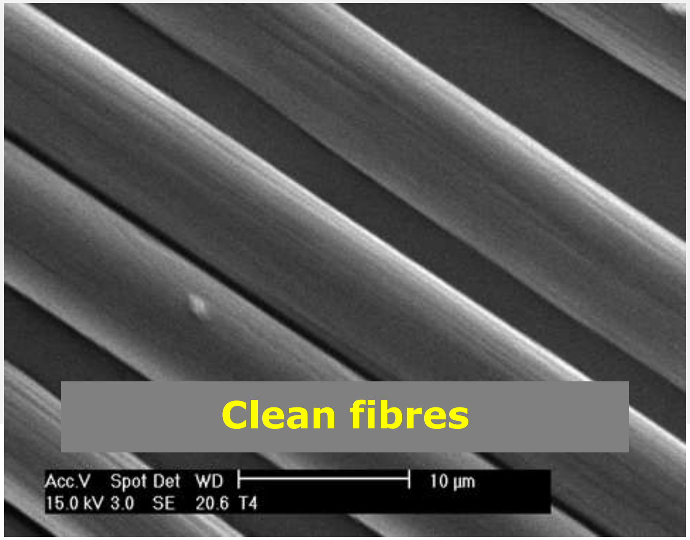


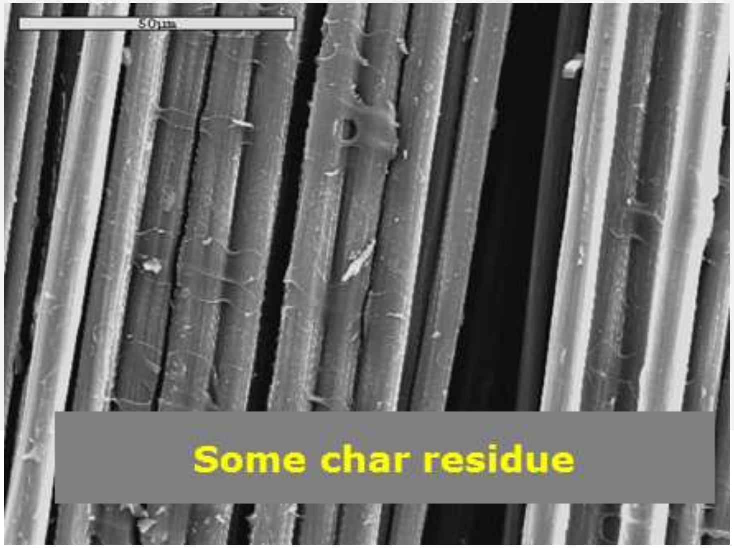


Section:02 Carbon Fibre Recovery

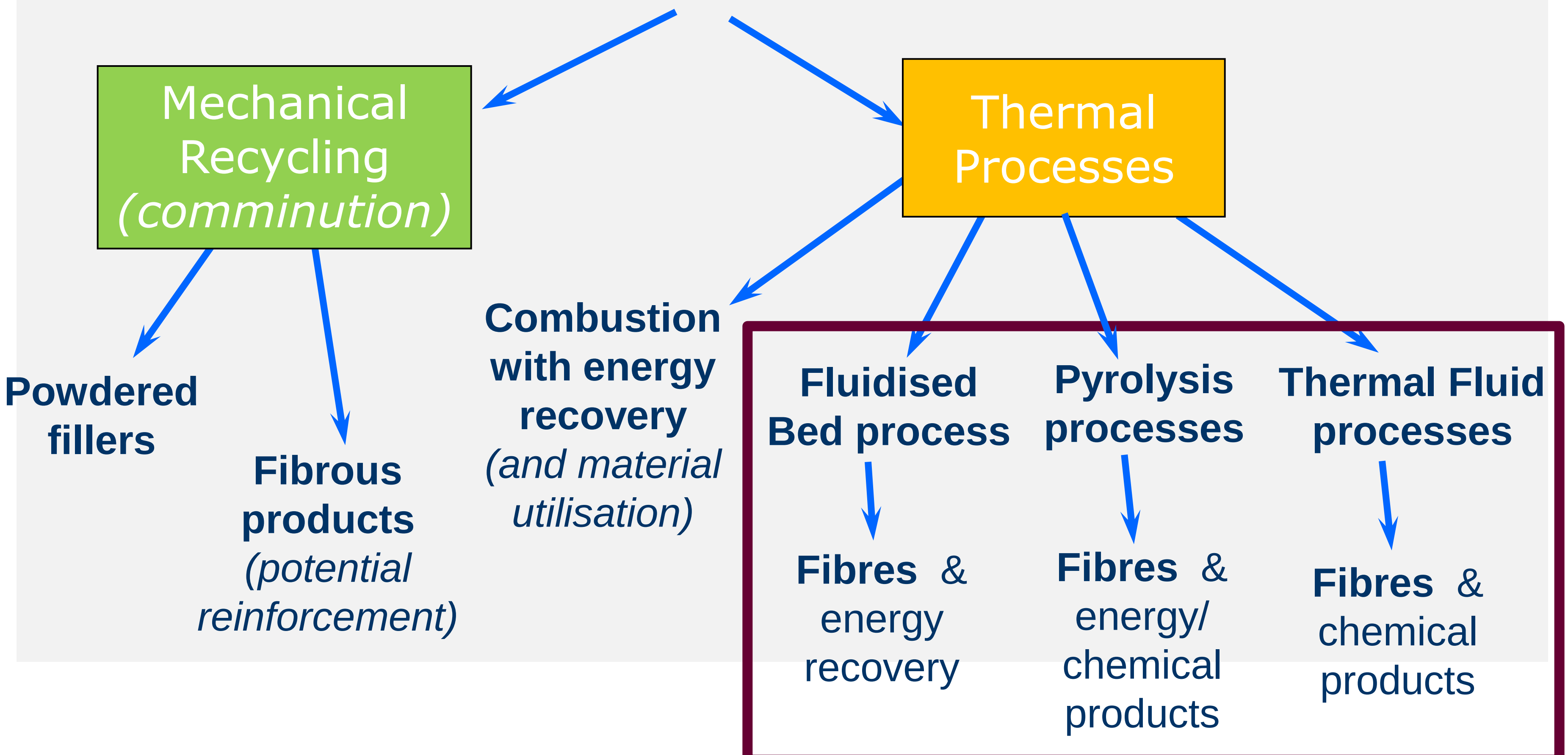
Fibre recovery processes – key issues

- Capability to process varied forms of waste
  - Mixed & contaminated
  - Different laminate thicknesses
- Cleanliness & form - suitability of rCF for further processing
- Polymer – energy recovery or recovery of chemical products



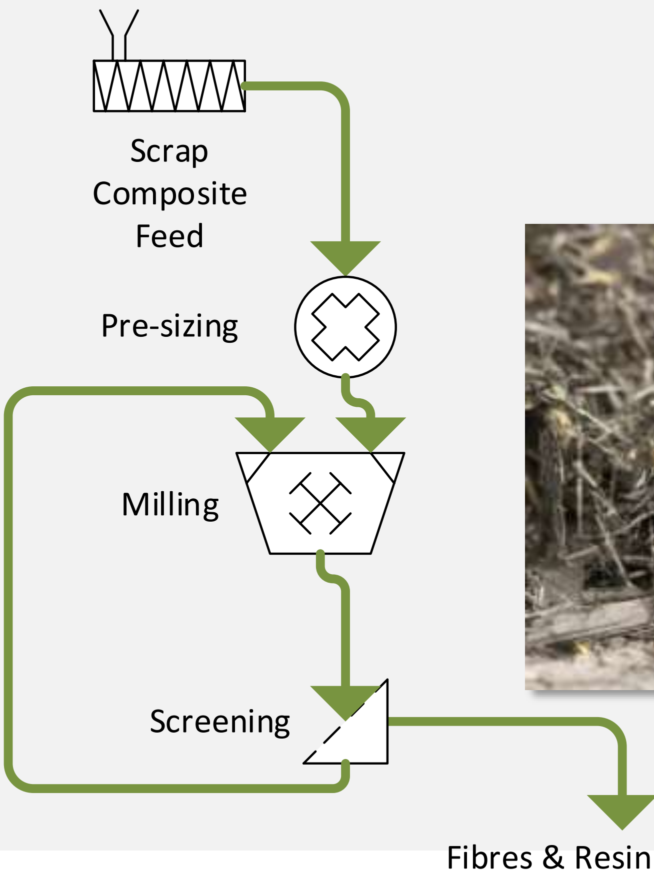


Recycling Processes for Thermoset Composites

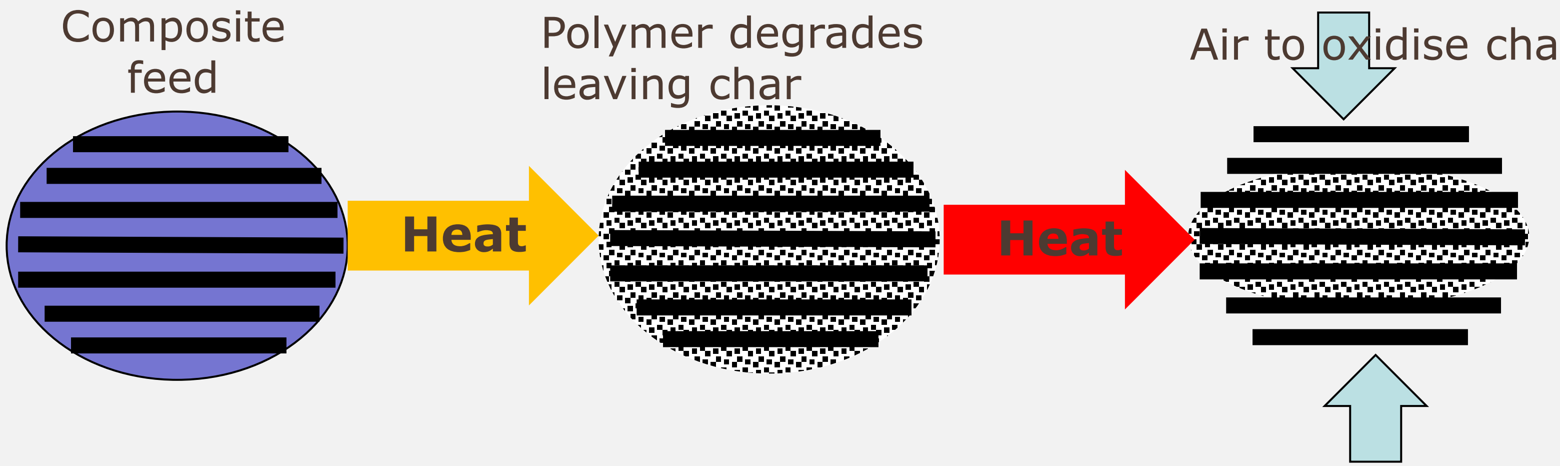


Mechanical Processes

- No resin removal stage
- Resin acts as a filler in final products
- Low cost & low energy usage
- Very poor mechanical properties
- Still R&D to do – hardware durability, minimising production of dust



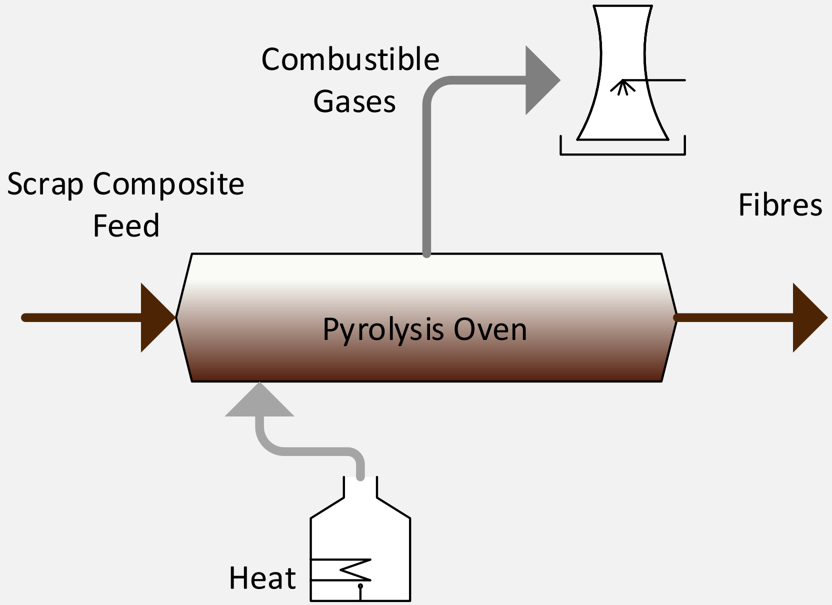
Thermal Recycling processes



Pyrolysis Processes:
Waste is heated in low oxygen conditions and pyrolytic char remains on fibres. Oxygen is introduced to oxidise the char. Care needed to ensure all char is removed without oxidising rCF.

Fluidised Bed Process:
As char is oxidised, fibres are released and elutriated from the bed. This avoids excess oxidation of fibres after char removal and only clean fibres are elutriated.

Pyrolysis processes

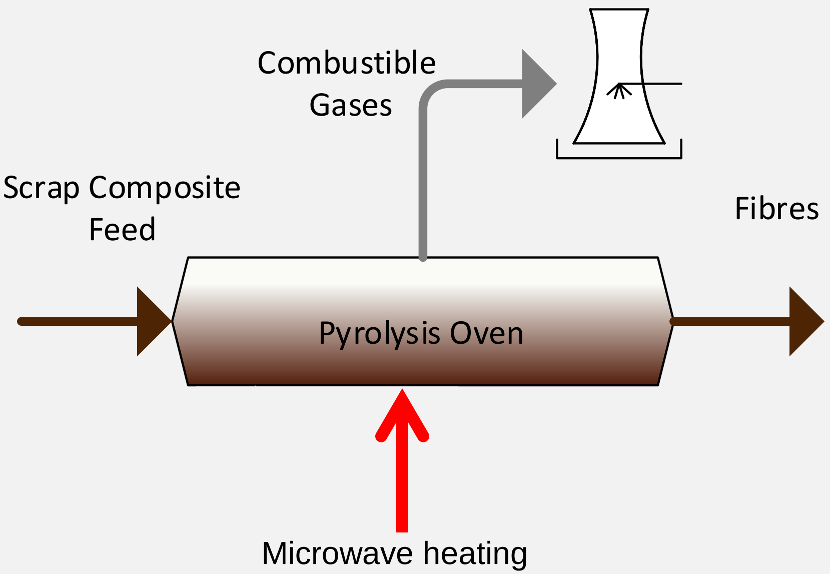


- Heating in absence of air
- Potential for low fibre oxidation
- Need to avoid char on fibres:
  - *Controlled atmosphere (O_2)*
- Operating commercially *(ELG CF UK/ MIT USA/ CFK Valley Germany/....)*

Key Issues:

- Controlled removal of pyrolytic char to ensure quality.
- Fibre length control: before or after pyrolysis?

Microwave pyrolysis?

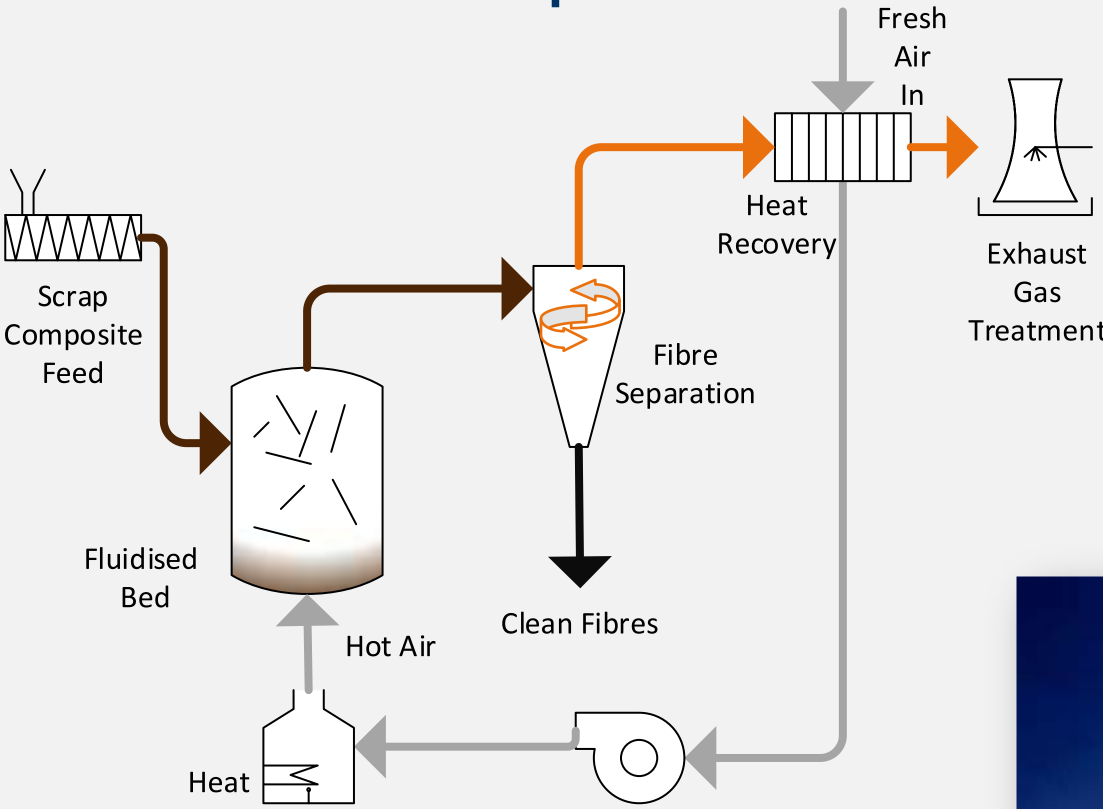


- Heating from microwave radiation
- Heating in absence of air
- No pyrolytic char formed on fibres
- No fibre oxidation damage
- Waste must be shredded and fragments disperse.

Key Issues:

- Difficult to control energy input and ensure full polymer removal
- Difficult to control process temperature

Fluidised bed process



- Recovery of clean carbon fibres
- Energy recovery from polymer
- Separates carbon fibre from contaminated and mixed materials *e.g. end-of-life waste*
- Robust process

Key Issues:

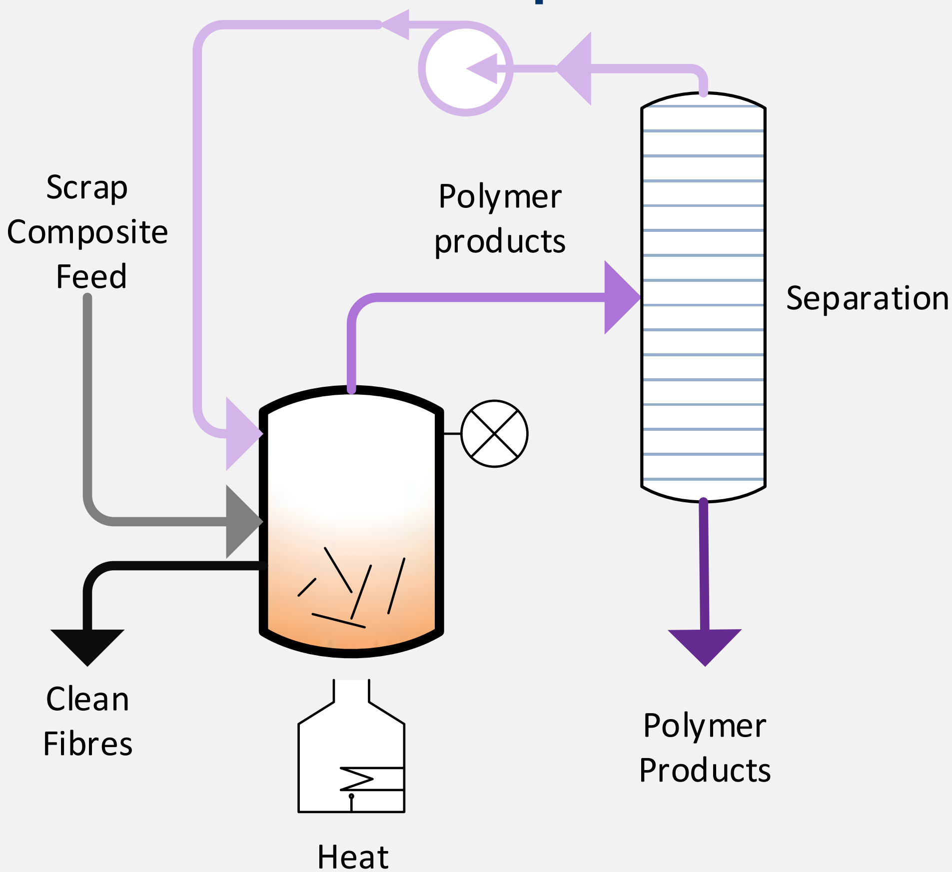
- Removal of contaminants from fluidised bed.
- Requires source of hot air *(heat recovery)*

Fluidised bed process - commercialisation

Fluidised Bed current trials

- What feed rate can we achieve?
- What is the corresponding energy usage?
- Process issues for long term operation – process automation
- Coping with real feed materials - very wide size distribution observed

Thermal-fluid processes



- Heating in presence of a fluid to breakdown and extract polymer aka solvolysis
- Supercritical fluids (propanol/water)
- Clean/ high grade fibres recovered
- Useful chemical products recovered

Key Issues:

- High pressure/temperatures – expensive equipment

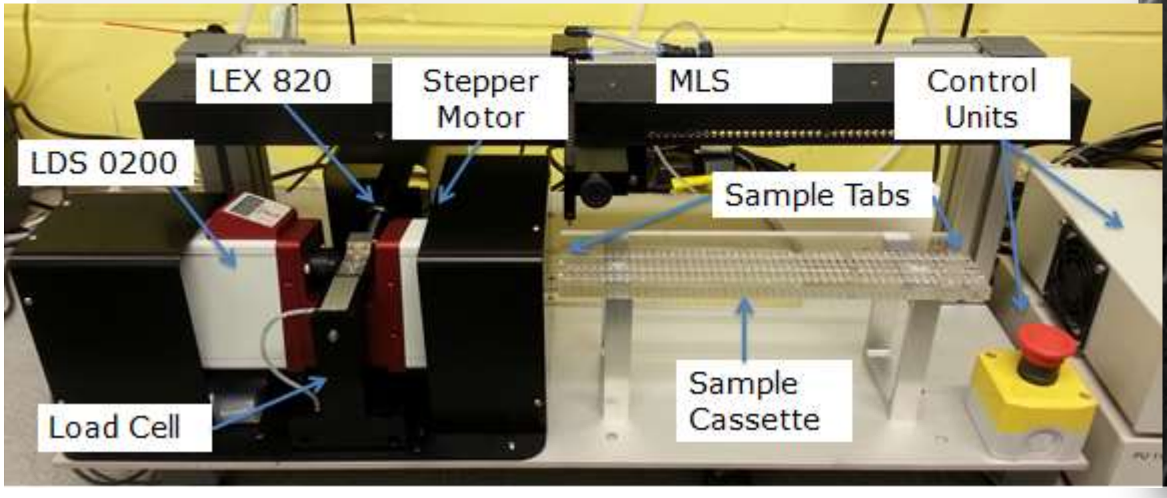
Thermal-fluid processes

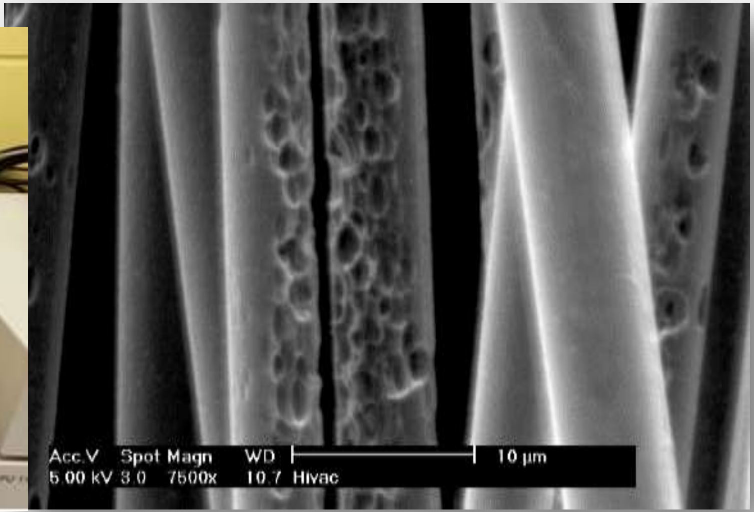
- Various decomposed polymer products obtained from SC Propanol Recycling Process
- Gas Chromatography with Mass Spectrometry
- Still unclear how much the products depend on the matrix material

Chemical Species	%
Phenol	34.9
p-isopropylphenol	26.4
p-isopropenylphenol	18.1
m-methylphenol	6.5
m-ethylphenol	4.7
Other	9.4

Mechanical properties of rCF

- Fibre **stiffness** generally similar to virgin – all processes
- Some degradation in **strength**
  - Thermal fluid processes show very little loss in strength <3%
  - Pyrolysis processes show up to 10% or more loss in strength *(dependent on processing conditions – see below)*
  - Fluidised bed process shows loss in strength of 25% to 50%. (But suitable for end-of-life and mixed/contaminated materials)

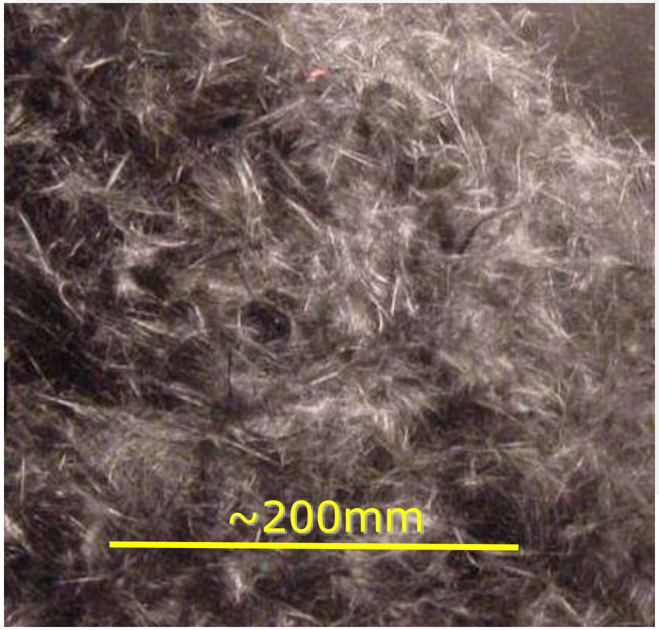


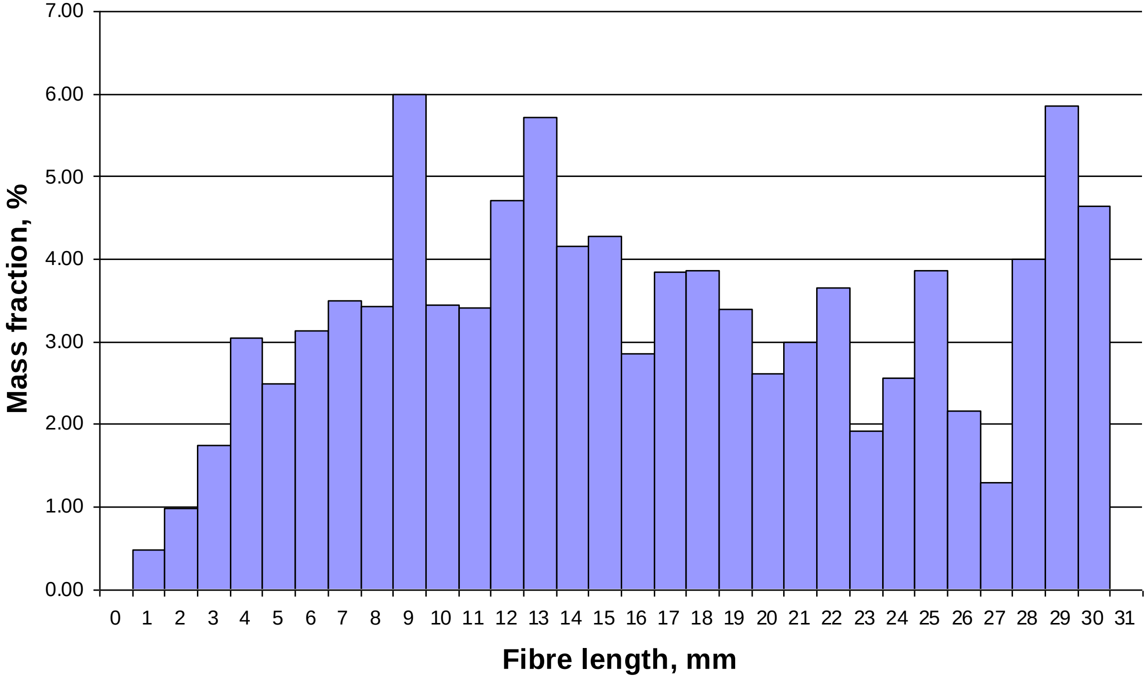


Physical form of rCF

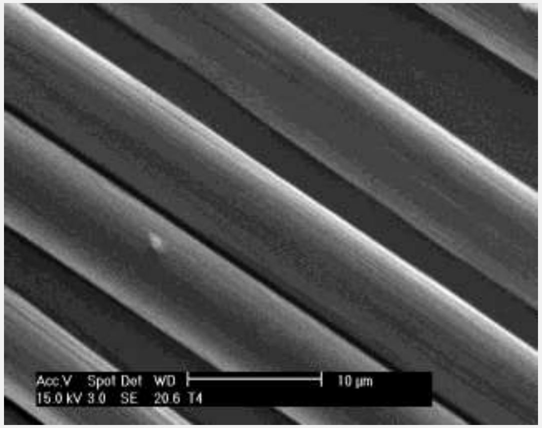
- Depends on whether fibres are reduced in length before, during or after the recovery process – pros & cons…
  - Length distribution
  - Fluffiness / bundle integrity

Recycled Carbon Fibre Ltd





Surface chemistry of rCF



- All processes *can* produce clean fibre
- Available data shows that recycled fibres generally give excellent interfacial shear strength with epoxy resin

T600S	**Virgin** *(sized)*	**Virgin** *(unsized)*	**Recycled** Fluidised Bed	**Recycled** SC propanol
Carbon*	58.9 %	66.8%	57.2 %	71.0%
C-OH	26.2 %	21.3%	29.1 %	17.7%
C=O	7.9 %	5.66%	6.8 %	5.17%
COOH	3.3 %	3.4%	3.9 %	3.2%
CO_3^{2-}	2.8 %	1.2%	2.5 %	1.5%

Electrical properties of rCF

- Electrical conductivity similar to virgin fibre
- Fibre can be effectively used for conducting polymers / EMI shielding

	Prepreg T600s		Filament Wound MR60H		
	Virgin	Recycled	Virgin	Recycled	
Resistivity $\times 10^{-3}\ \Omega$ cm	**1.90**	**1.81**	**1.75**	**1.47**	*±0.15*

Conclusions – Recycling processes

- Pyrolysis remains the dominant commercial process
- Solvolysis and fluidised bed may grow to commercial scale

- Improved processes may well appear!
  - Improved utilisation of resin products in the short to medium term
  - Improved fibre properties
  - Reduced char levels
  - Improved bundle integrity in the longer term – improved in-process utilisation

- Current efforts at improvement are limited by available sales avenues for fibres – limited markets to sell into & development of re-use processes still required

- Costs of technology transfer & commercialisation are high

Section:02
Questions?

Section:03
Fibre re-use

Key recovered fibre re-use issues

- Current situation is problematic – if material is not available then processes will not be developed
- R&D areas reasonably well defined by aerospace and automotive requirements

- Key questions
  - Funding of commercialisation?
  - Value of fibres and intermediates?
  - Overall approach (fibres, tow pellets, mat, prepreg, compound etc)

Virgin vs. Recycled CF markets

- Normally rCF is not the same as virgin CF
- What should be our approach for re-use of carbon fibres?

1. Direct **competition** with virgin materials
    - Reduced mechanical performance offset by reduced cost
    - At what level will we compare ? Tow, mat, compound?
2. **New markets**
    - New material forms (e.g. commingled)
    - Glass replacement
3. Increased **functionality**
    - With virgin fibre smaller tow sizes are more costly
    - Enhanced drape
    - Conductivity

Problems with fibre form

- Currently fibre consistency is not always adequate for downstream processing due to residual char – particularly an issue for higher performance / value products

- Fibre form is challenging!
  - Low density
  - 3D random
  - Discontinuous
- Mechanical property degradation

Measurement of fibre quality

- Recovered fibre difficult to test using existing standards
  - SFTT sometimes possible

- Fibre dispersability important
- Char levels critical to re-use
- Fibre length measurement required
- Fibre mechanical property measurement required

- Currently developing an approach using a slurry of fibres in a viscous liquid