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Pyrolysis - Sustainable waste treatment with negative carbon balance

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OUTLINE

- Objective-Motivation
- Biomass
- Thermochemical Conversion Processes
  - Pyrolysis
- Pyrolysis Products
  - Bio-oil
  - Bio-char
- Conclusion

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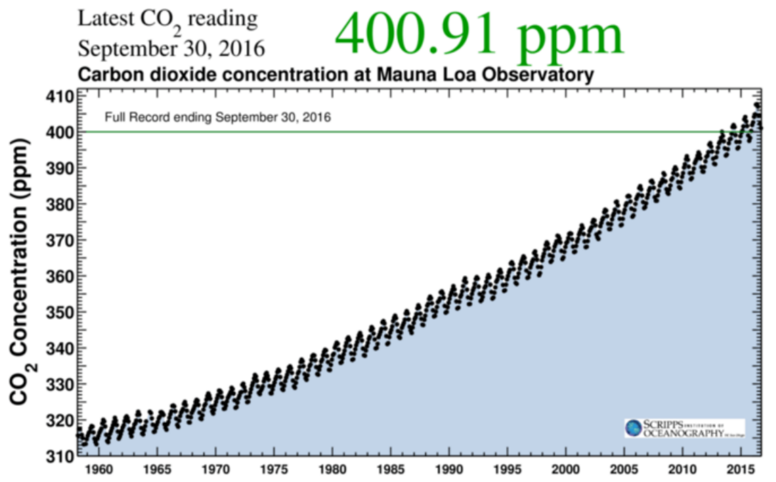
Objective-Motivation

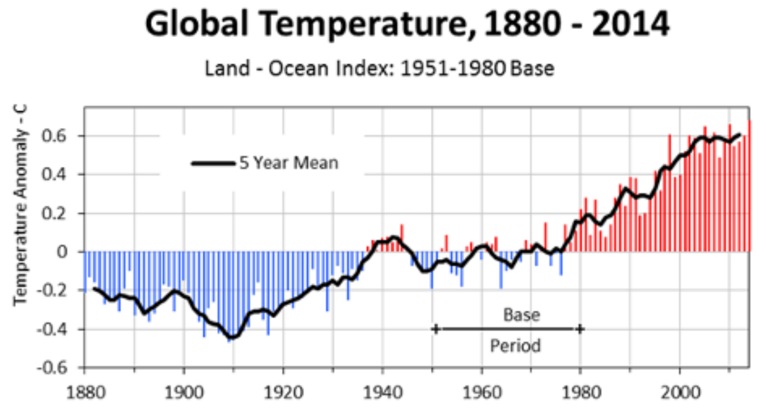
According to WHO:

- Over the last 50 years, human activities have released sufficient quantities of CO_2 and other greenhouse gases to trap additional heat in the lower atmosphere and affect the global climate.
- In the last 130 years, the world has warmed by approximately 0.85°C. Each of the last 3 decades has been successively warmer than any preceding decade since 1850.
- Sea levels are rising, glaciers are melting and precipitation patterns are changing. Extreme weather events are becoming more intense and frequent.

http://www.who.int/mediacentre/factsheets/fs266/en/

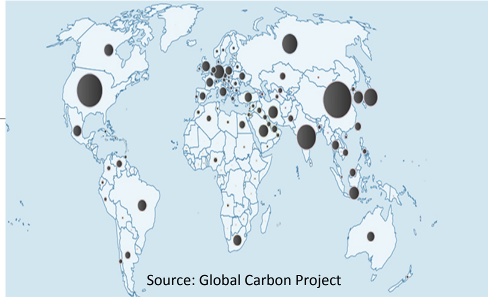


Atmospheric carbon dioxide concentrations, recorded by the Mauna Loa Observatory in Hawaii. The line is jagged because CO2 levels rise and fall slightly each year in response to plant growth cycles. Scripps Institute of Oceanography



Source: Goddard Institute for Space Studies (GISS) and Climate Research Unit (CRU), prepared by ProcessTrends.com, updated by globalissues.org

Objective-Motivation

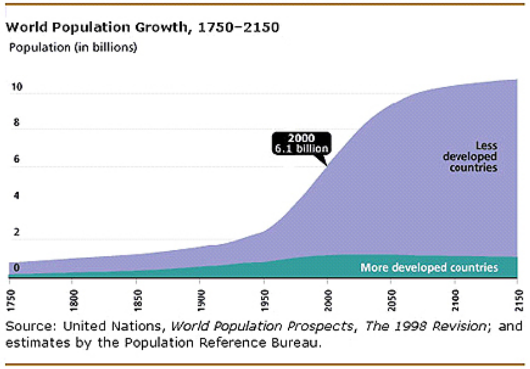


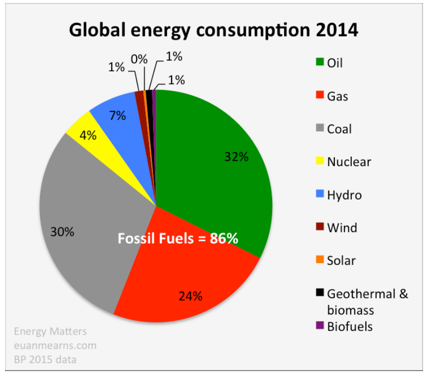
Increasing energy demands

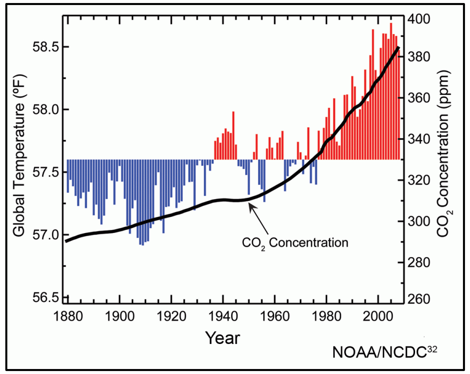
Fossil fuel consumption

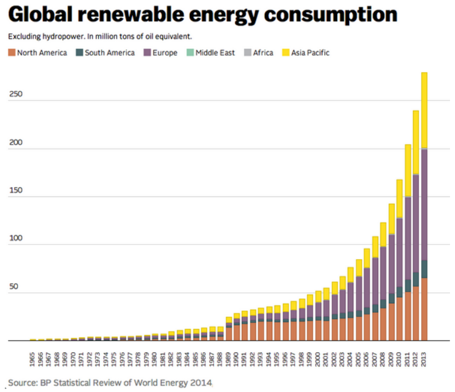
Increase in the atmospheric CO_2

Utilization of renewables





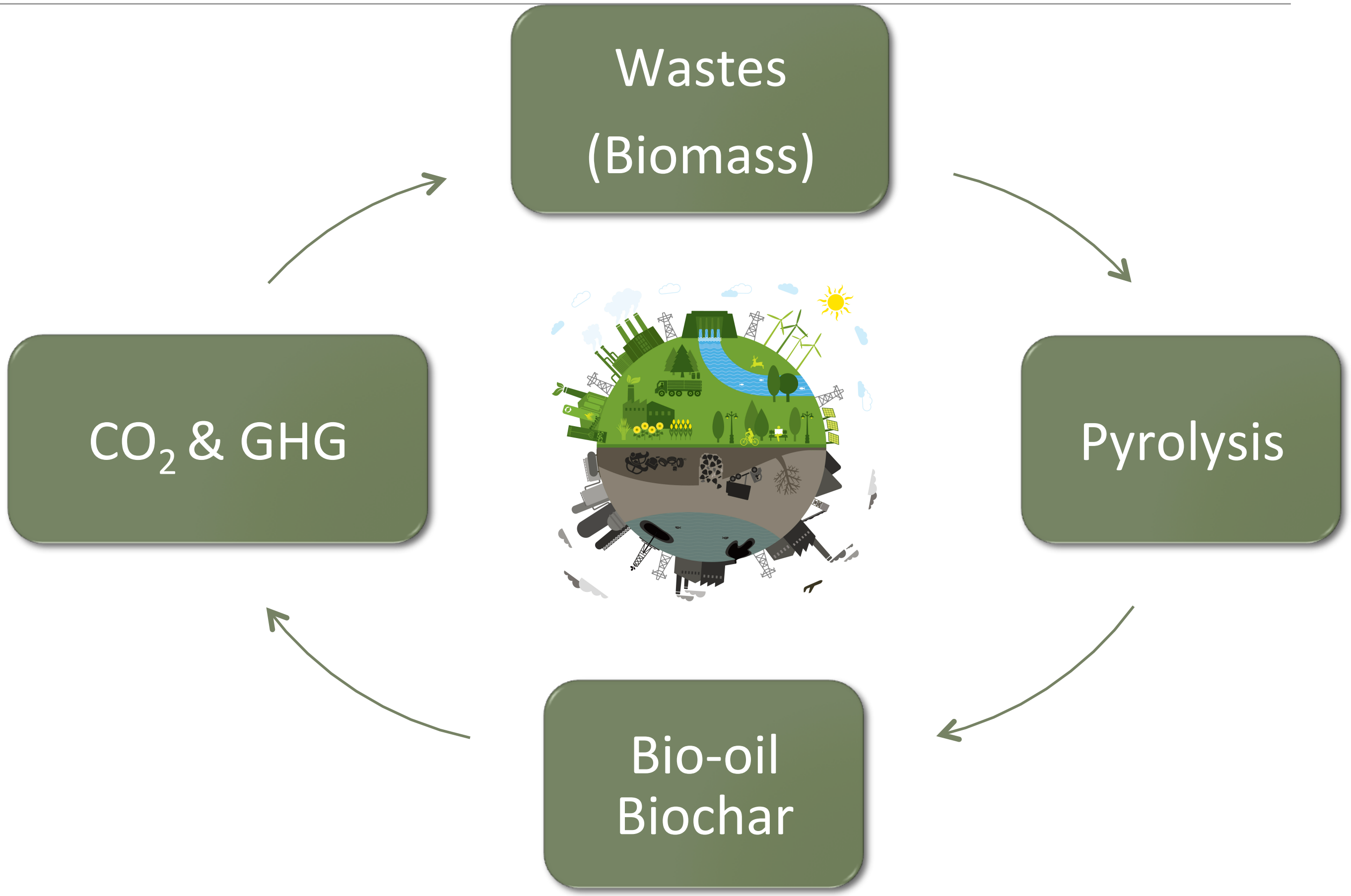




Objective-Motivation

Utilization of Renewables:

- Solar
- Wind
- Geothermal
- Wave
- Biomass



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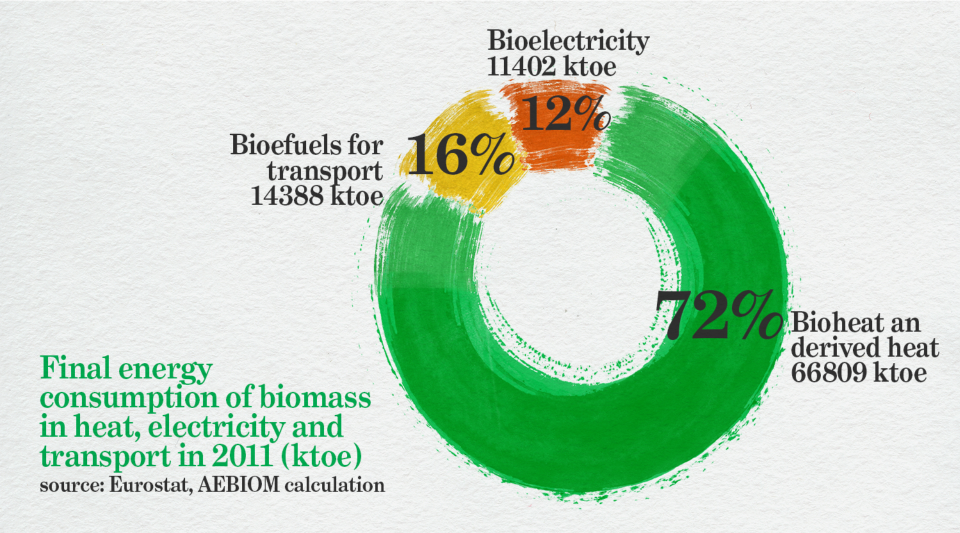
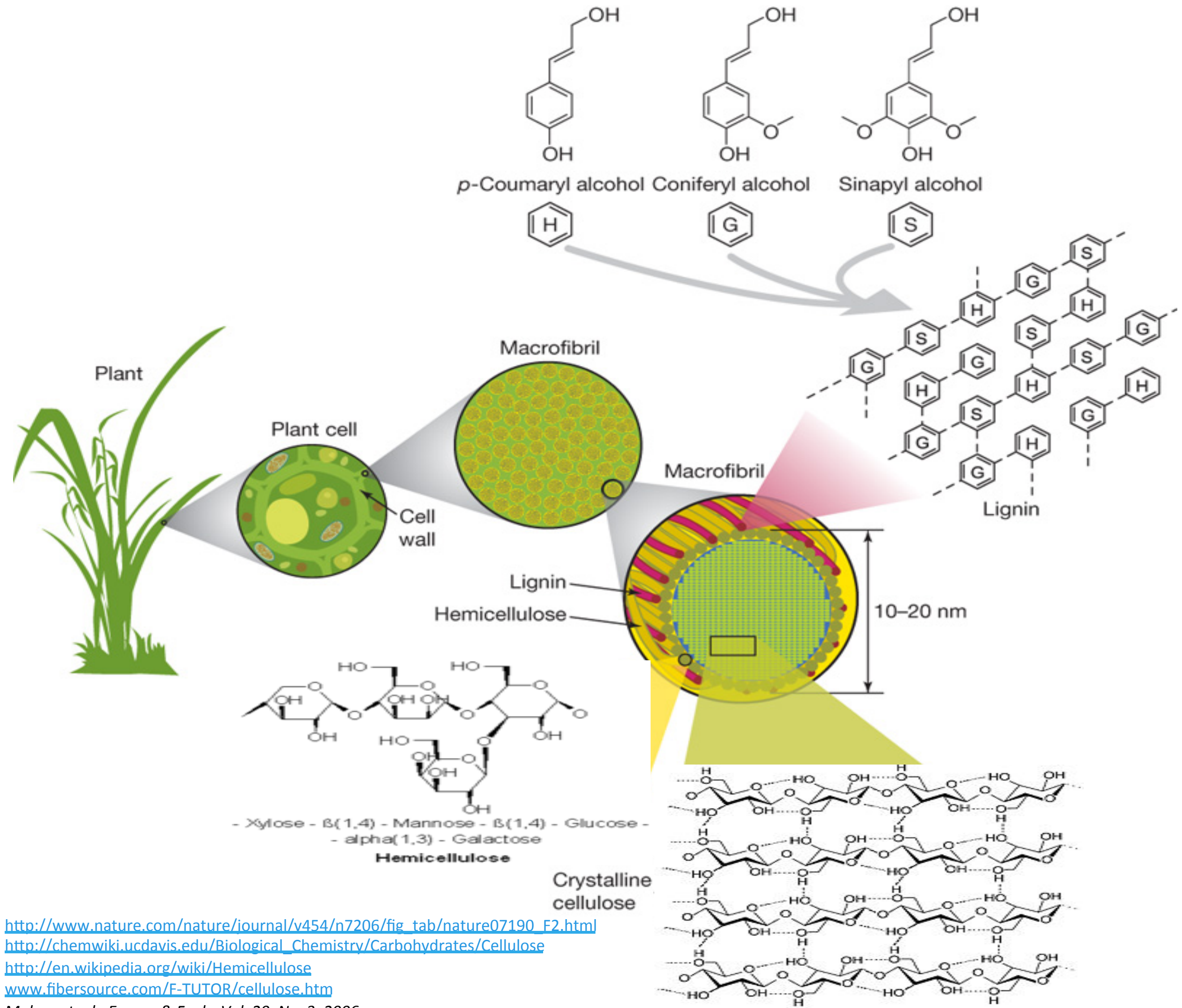
Understanding Biomass

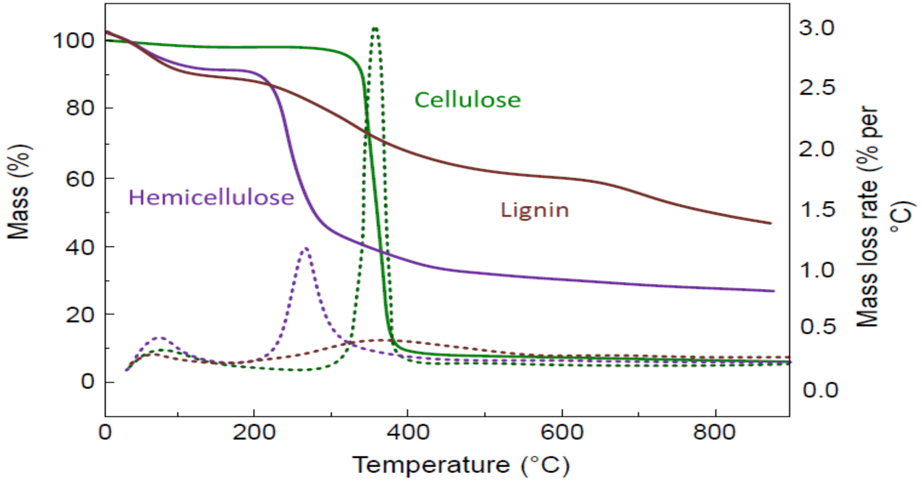
Biomass ??? Waste



Components and thermal degradation of lignocellulosic biomass



http://www.nature.com/nature/journal/v454/n7206/fig_tab/nature07190_F2.html
http://chemwiki.ucdavis.edu/Biological_Chemistry/Carbohydrates/Cellulose
http://en.wikipedia.org/wiki/Hemicellulose
www.fibersource.com/F-TUTOR/cellulose.htm
Mohan et. al., Energy & Fuels, Vol. 20, No. 3, 2006



Hemicellulose

- Thermal decomposition: 200-260 °C
- Produces more volatiles, less tar, and less char than cellulose.

Cellulose

- Thermal decomposition: 200-350 °C
- Produces mainly CO, CO_2 , H_2O and lower molecular weight hydrocarbon gases,
- Produces more tar than hemicellulose, less char than lignin.

Lignin

- Thermal decomposition: 230-500 °C.
- Lignin is more difficult to dehydrate than cellulose or hemicelluloses.
- Produces more residual char than does the pyrolysis of cellulose.

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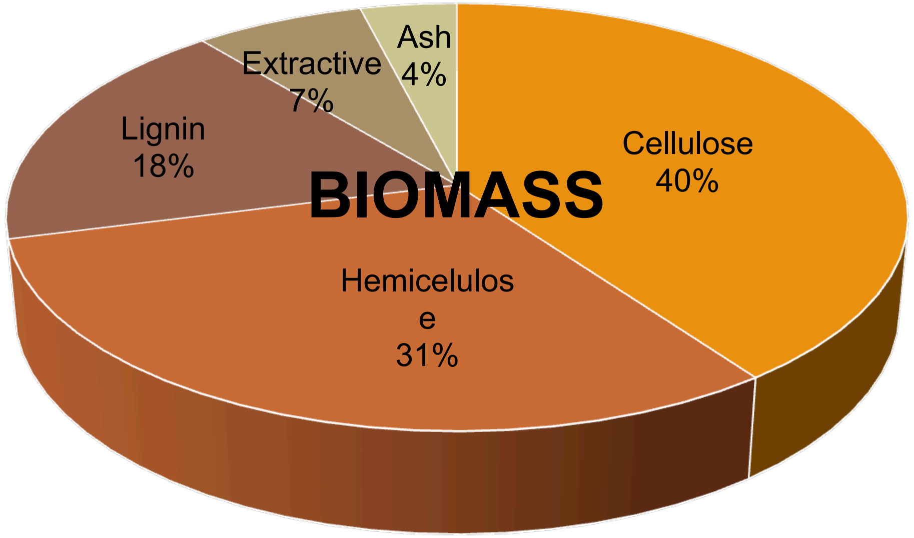
BIOMASS TYPES

Herbaceous and agricultural wastes

Forestry residues: wood and woody biomass

Energy crops

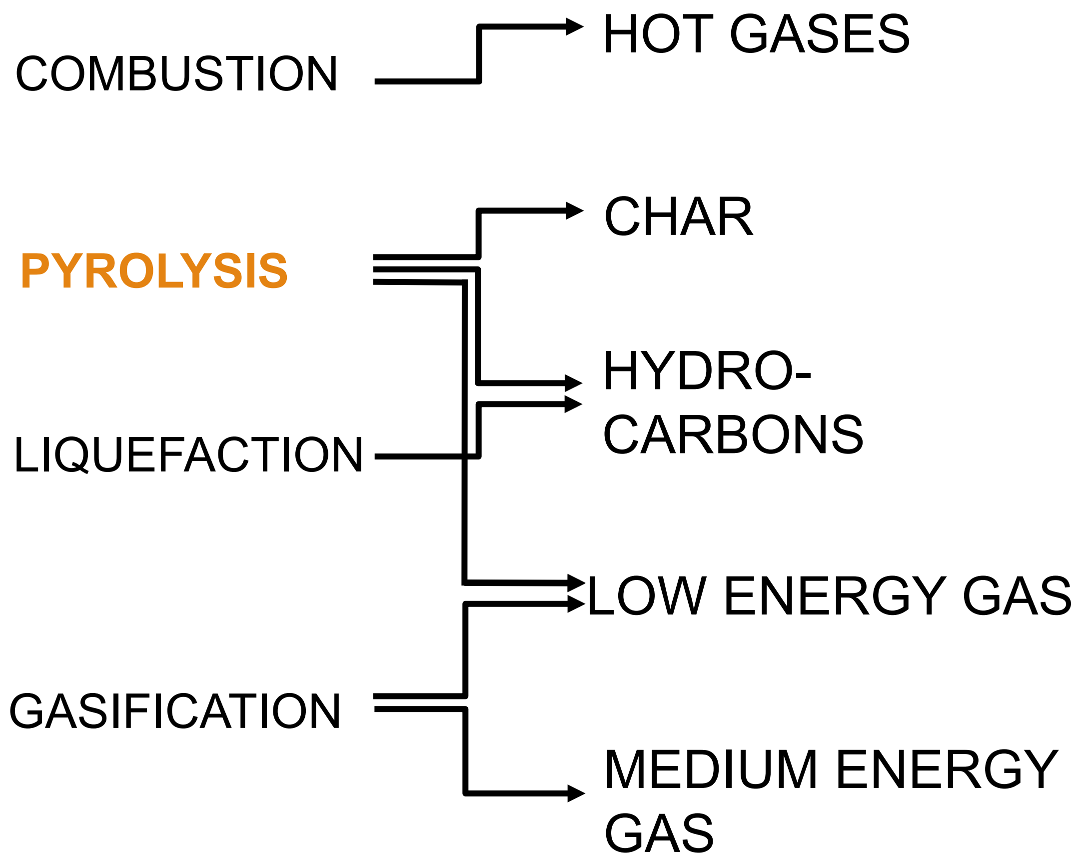


Animal and human wastes

Contaminated and industrial wastes

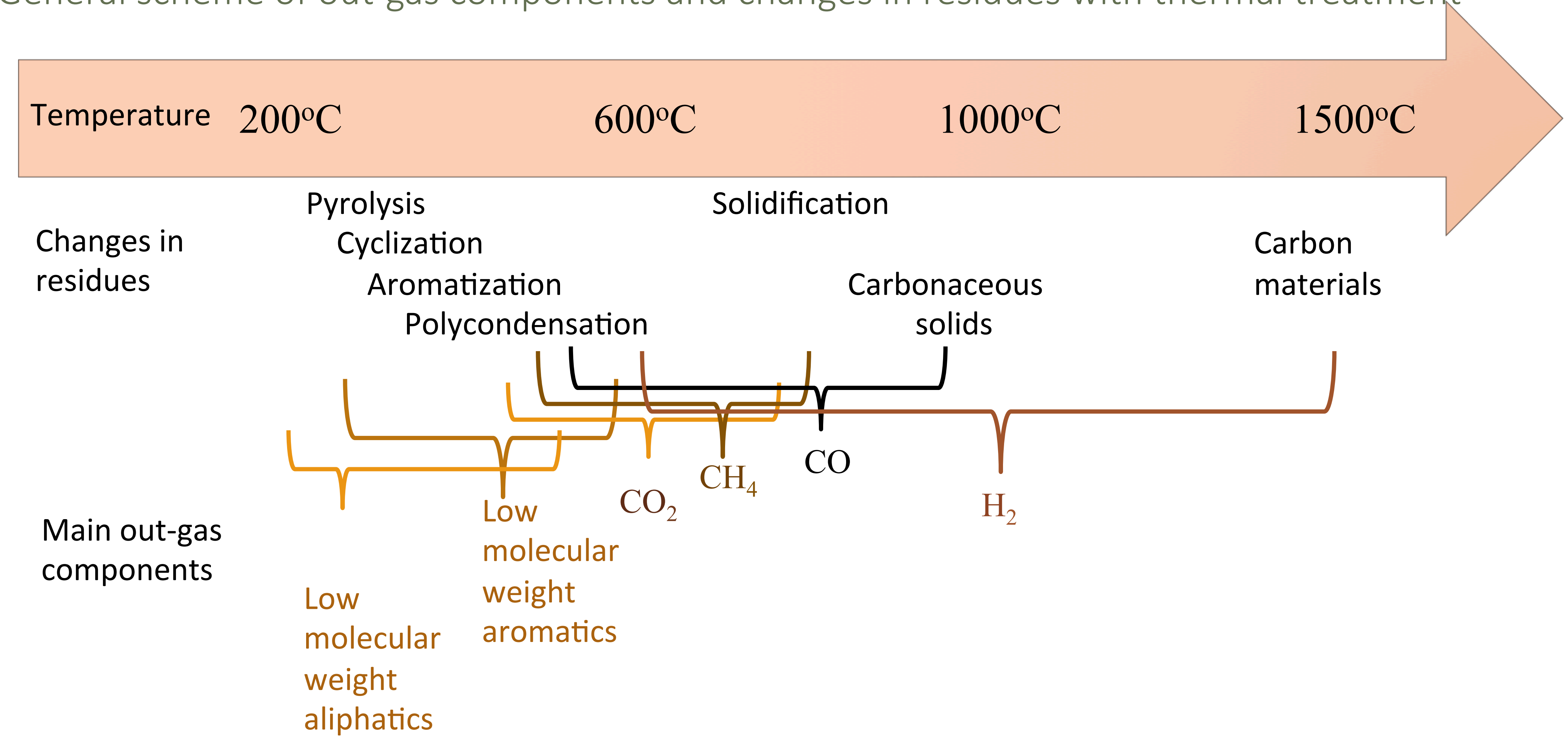
THERMOCHEMICAL CONVERSION PROCESSES

PRODUCTS



Thermal decomposition of biomass

General scheme of out-gas components and changes in residues with thermal treatment



Michio Inagaki, New Carbon Materials, pp.124

Typical process conditions and product yields for pyrolytic processes

	Fast pyrolysis	Slow pyrolysis (Carbonisation)	Torrefaction (partial slow pyrolysis)
Temperature	~ 500°C	> 400°C	< 300°C
Heating rate	Fast, up to 1000°C/min	Slow, 5-80°C/min	-
Reaction time	Few seconds	Hours to days	< 2h
Pressure	Atmospheric (and vacuum)	Atmospheric (or up to 1 MPa)	Atmospheric
Medium	Oxygen-free	Oxygen-free or oxygen-limited	Oxygen-free
Typical product yields (wt. %)			
Bio-oil (wt %)	75	30	5
Char (wt%)	12	35	80
Gases (wt.%)	13	35	15

Ref.: Ronnse, F. (2016), Bridgwater (2012); van der Stelt *et al*. (2011); Williams and Besler, (1996); Bain and Broer (2011); Nachenius *et al*. (2013); Kambo & Dutta,(2005).

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Bio-oil

- Fuels
  - Hydrogen
  - Upgrading
  - Fuel via syngas
- Chemicals
  - Resins
  - Flavours
  - Adhesives
  - Phenolics
- Heat
  - Cofiring of boiler and furnace
- Power
  - Diesel Engine
  - Turbine

Properties of bio-oil

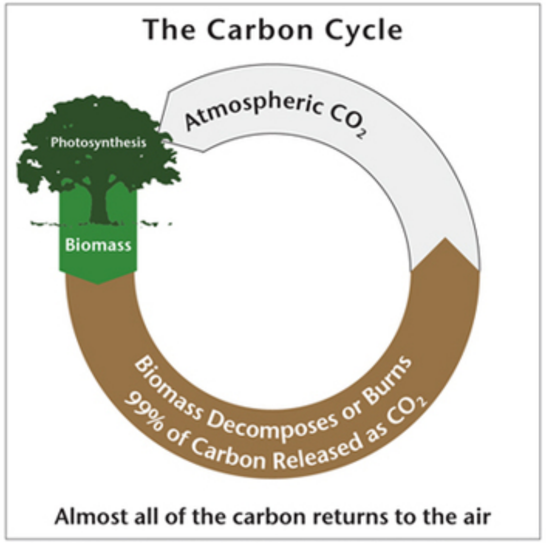
Property	Bio-oil	Light Fuel Oil	Heavy Fuel Oil
Moisture content (wt.%)	15-30	-	0.1
Ash content (wt.%)	<0.02	<0.01	0.03
Specific gravity	1.2	-	0.94
pH	2-3	-	-
Viscosity at 50 °C (centistokes)	7	4	50
Pour point (°C)	-33	-15	-18
Distillation residue (wt.%)	<50	-	<1
Higher heating value (MJ/kg)	20-30	35-37	38-40
Elemental composition (wt.%)			
C	54-58	-	85
H	5.5-7.0	-	11
N	0-0.2	0	0.3
S	Negligible	0.15-0.5	0.5-3.0
O	35-40	-	1.0

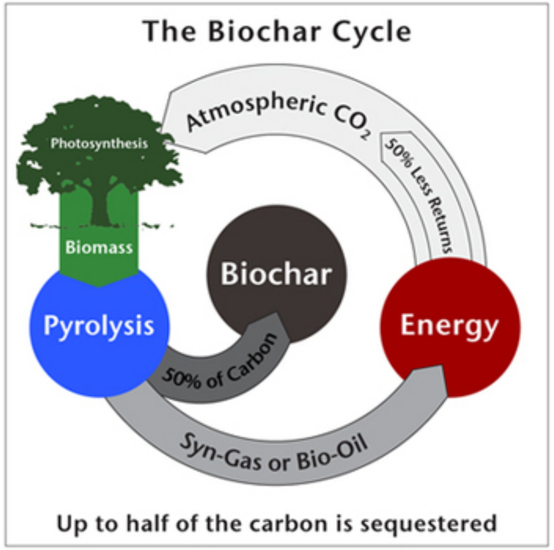
Czernik and Bridgwater, 2004;
Mohan et al., 2006

Effect of process conditions on bio-oil yields for various biomass samples

Biomass	Pyrolysis Temperature (°C)	Reactor type	Heating rate (°C/min)	Pyrolysis atmosphere	Catalyst	Maximum bio-oil yield (wt.%)	Heating Value (MJ/kg)	Reference
Pinewood sawdust	500	Conical spouted bed reactor	Fast pyrolysis	Nitrogen	--	75.0	14.6 (Lower heating value)	Amutio et al., 2012
Hard wood or soft wood feedstocks	450	Tubular vacuum pyrolysis reactor	Slow pyrolysis	Nitrogen	--	50.0-55.0	--	Ortega et al., 2011
Rice straw	550	Fixed-bed reactor	5	Steam	--	35.86	32.58	Pütün et al., 2004
Apricot pulp	550	Fixed-bed reactor	5	Steam	--	27.7	35.63	Özbay et al., 2008
Olive residue	500	well-swept and high-speed heated fixed-bed batch reactor	500	Nitrogen	--	46.72	29.6	Pütün et al., 2009
Euphorbia rigida	550	Fixed-bed reactor	7	Static	Criterion-534	30.98	--	Ateş et al., 2005

Biochar
Slow Pyrolysis and Carbonization





Non-graphitizable carbonaceous solid residue after pyrolysis.

Char

- Solid synthetic fuels
- Bio-oil/char slurry
- Adsorbents
- Substrate for catalysts

Bio-char

- C sequestration
- Soil conditioning via changes in soil chemistry
- Soil amendment

Ref.: Biochar solutions Inc., 2011

Biochar Production: Effect of various parameters

Parameters		Degree	Expected result
Feedstock related	Hemicellulose+Cellulose	Low (<55 %)	Less volatiles, more biochar
	Lignin	High (>35 %)	
	Ash	High (>8 %)	
	Moisture content	Low (<10 %)	
	Particle size	Low (< 2 mm)	More heat transfer, rapid decomposition, less biochar
Process related	Batch	-	More residence time, more biochar
	Continuous	-	Less residence time, rapid heating, more bio-oil
	Heating rate	Low (< 10°C/min) High (> 300°C/min)	Slow heating, more biochar Rapid heating, more bio-oil
	Pyrolysis/Carbonization Temperature	Low (<400 °C) Moderate (~500 °C) High (>700 °C)	More biochar, less C content in biochar Less biochar, more C content in biochar Less biochar, more gas products
	Residence Time*	Low (0<t<10 min) High (>1 h)	Less carbonization and more C content in biochar More carbonization and more C content in biochar

* Residence time refers to the holding time of biochar at the final pyrolysis temperature.

Biochar Production: Examples from previous studies

Biomass type	Reactor type	Biochar production techniques	Biochar production temperature (ºC)	Heating rate (C min⁻¹)	Reaction time (min)	Yield (%)	C (wt. %)	Surface area $m^2\ g^{-1}$	Reference
Pine Cone Soybean Cake Corn Stalk Peanut Shell	Fixed-bed reactor	Slow pyrolysis	550	10	--	29.6 25.2 24.9 29.7	95.16 83.95 94.97 93.61	208 2.1 11.8 211	Apaydin-Varol and Pütün, 2012
Tea Waste	Fixed-bed tubular reactor	Fast pyrolysis	400 500 550 700	300 300 300 300	10	43.4 35.7 30.2 21.1	--	2 - - 7.5	Uzun et al., 2010
Pistachio shell	Fixed-bed tubular reactor	Fast/slow pyrolysis	400 500 550 700 500 500 500 500	300 300 300 300 5 100 500 700	--	29.5 21.7 20.5 15.4 28.0 24.7 22.0 20.9	--	--	Pütün et al., 2007
Olive residue	Fixed-bed reactor	Slow pyrolysis	400 500 550 700	7	--	32.4 28.8 28.0 27.5	-- 69.34 -- --	--	Pütün et al., 2005
Rice straw	Fixed-bed reactor	Slow pyrolysis	400 500 550 700	5	--	30.5 27.6 26.1 23.6	--	--	Pütün et al., 2004

Biochar Characterization

- The International Biochar Initiative (IBI) biochar standards identify three categories (A, B and C) of tests for biochar materials.

  - Category **A** and Category **B** are for basic utility properties and toxicant reporting.
  - Necessary for all biochars.

    - particle size and moisture
    - elemental composition (H, C and N)
    - ash proportion
    - electrical conductivity
    - pH/liming ability.
    - the soil toxicity assessment thresholds.

  - The category **C** is optional and composed of advanced analysis and soil enhancement indicators.

    - volatile matter content
    - nutrient content
    - surface area

  - Other techniques recently studied…

    - Surface morphology
    - porosity
    - Surface chemistry- functional groups
    - CEC
    - ….

General experimental procedure

Feedstock

Oven dried and sieved

Pre-analysis

Ultimate, Proximate, TGA_FTIR_MS and Component analysis, ICP-OES

Slow Pyrolysis

400, 450, 500, 550 and 600 °C 10 °C/min,30 min residence time

Bio-oil

Separation to subfractions, transportation fuels,

Phenolic compounds

Biochar

High nutrient capactiy, Microporosity, Alkaline and Carbon structure

Biochar Anaysis

CHN analysis,pH, SEM,He pycnometer,

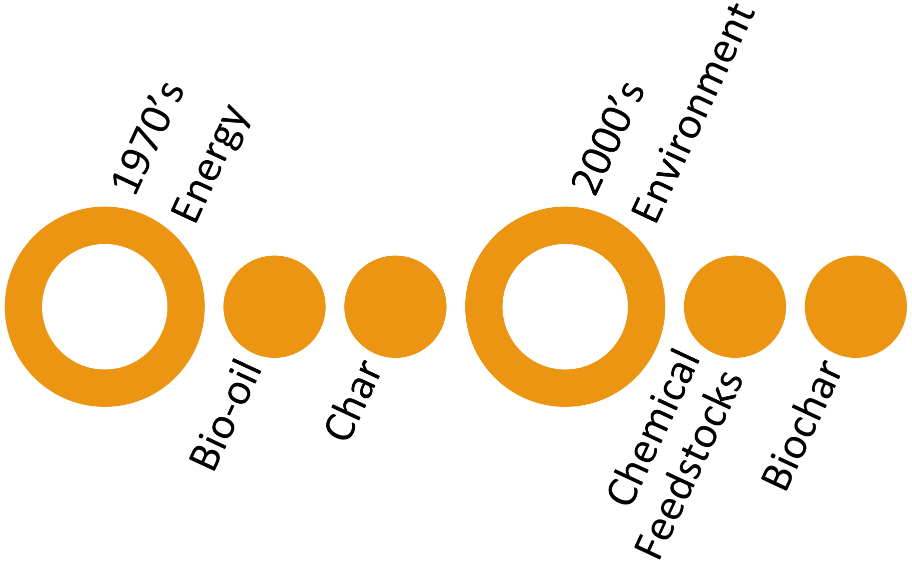
ICP-OES

Soil

Nutrient release, Contaminant adsorption, C sequestration, pH neutralizing

Conclusions and further remarks

Pyrolysis - Where are we now???



Pyrolysis – What is next???

Diversity of biomass samples and accordingly bio-oil and bio-char properties emphasises the need for a case-by-case evaluation of each product prior to its utilization.

Last year Prof. Basak Burcu Uzun passed away unexpectedly.
We have not only lost a colleague but a true friend.

Thank you for your attendance…

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