Microwave-assisted activation of biomass

15-11-19

Dr. Vitaliy Budarin

York

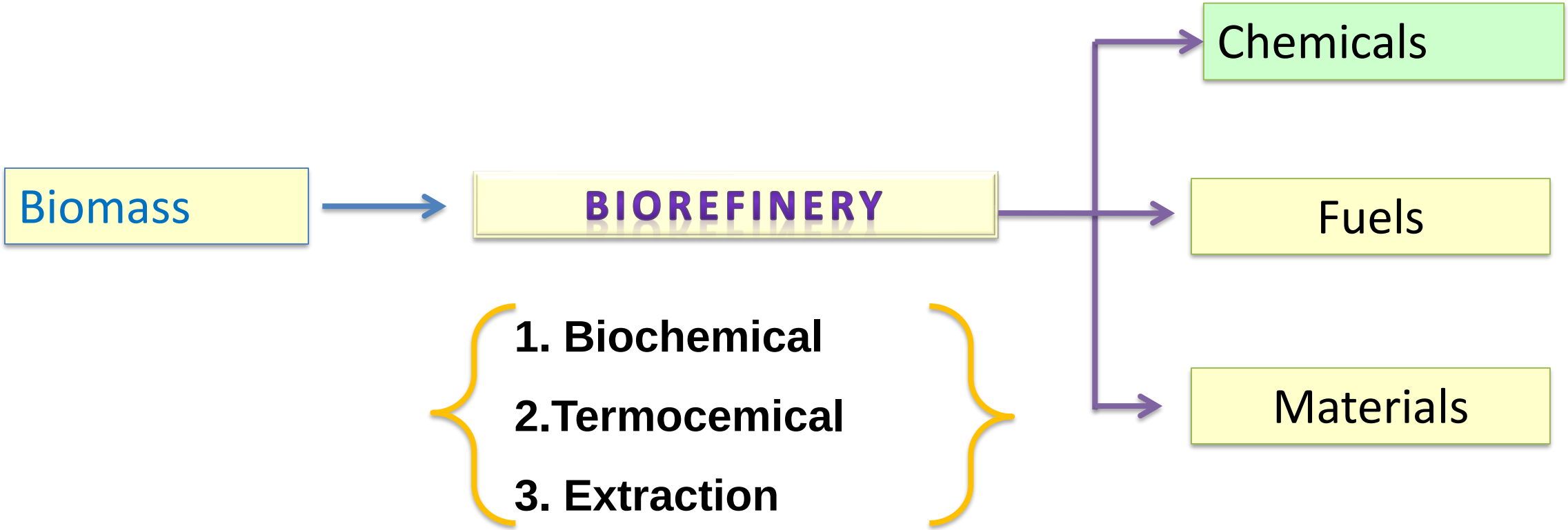
- **One of Europe's most beautiful and historic cities**

Green Chemistry Centre of Excellence

- **More than 80 peoples**
- **New building**

MAJOR FOCUS OF THE GROUP **: BIO-REFINERY**

Our motivation: Biorefinery concept

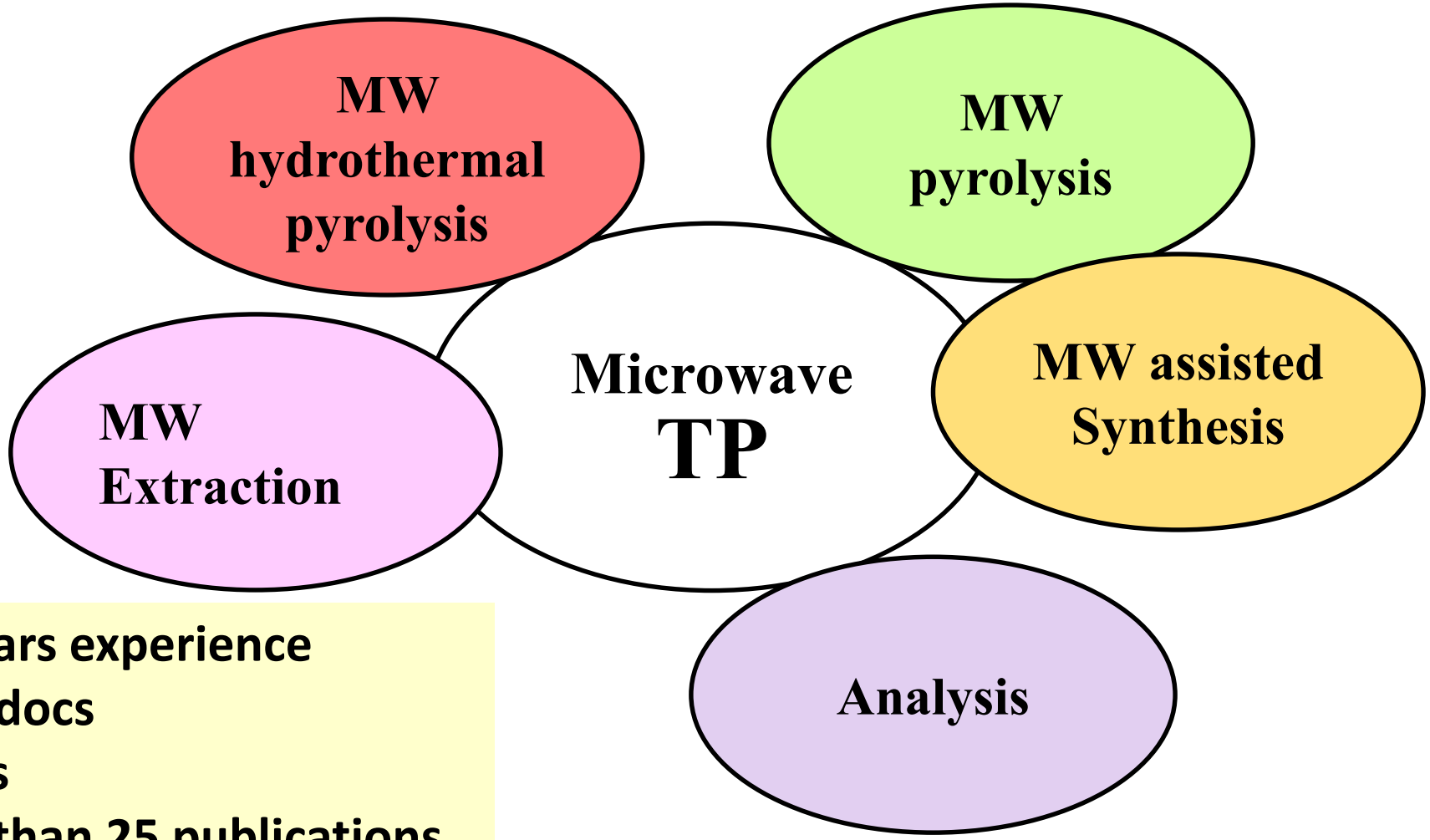


Biorefinery is "a facility that integrates conversion processes and equipments to produce fuels, power, and chemicals from biomass".

Green Technology of biomass utilization

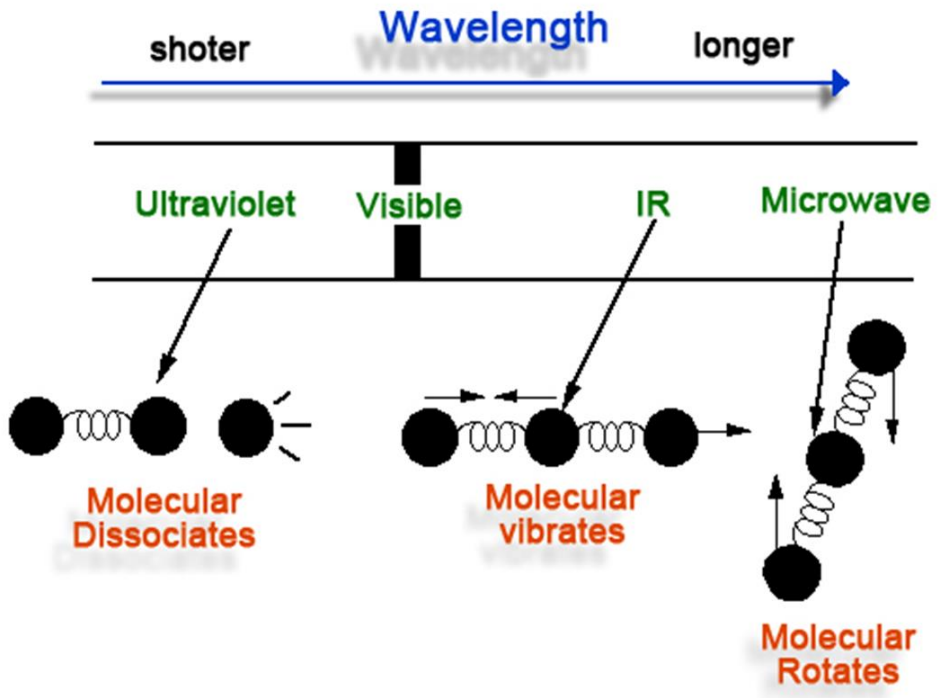
- **Alternative Solvents** (bio-solvents)
- **Clean Synthesis** (chemistry of platform molecules)
- **Microwave Chemistry** (bio-mass activation)
- **Renewable Materials** (materials from biomass)

Microwave Technology Platform (Microwave TP)



- >10years experience
- 3 postdocs
- 3 PhDs
- More than 25 publications
- 2 patents
- 3 patent applications

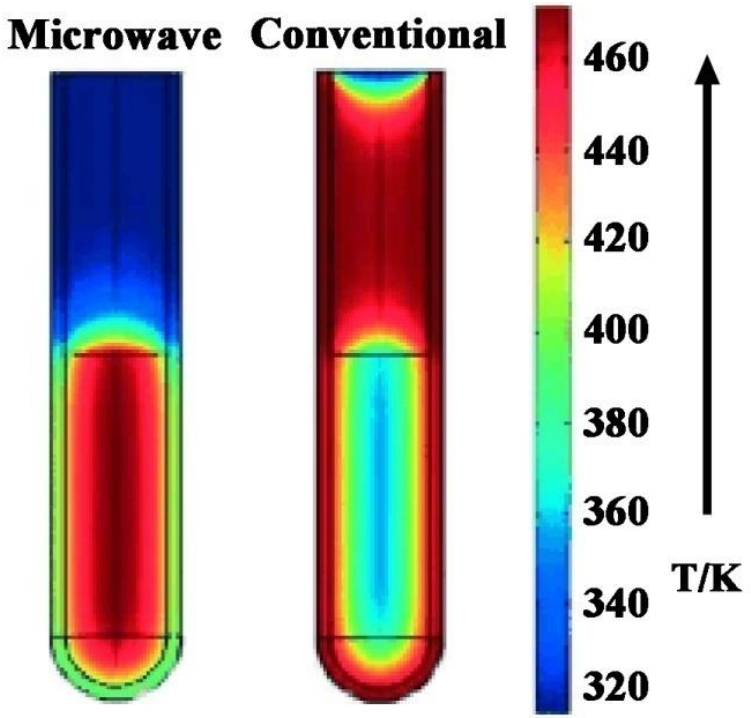
MW within electromagnetic spectrum



Parameter	Value
Electromagnetic Field frequency	2. 45 109 cm^{-1}
Wavelength	12.2 cm
Quantum energy	**0.037** kcal/mol

Hydrogen bond energy in water : **4.8** kcal/mol

Why Microwave? Advantages of MW heating



- ✓ **Rapid volumetric heating**
- ✓ **Uniform heating**
- ✓ **Instant control**
- ✓ **Acceleration of reaction rate**
- ✓ **Selective interaction with active groups**

Volumetric heating has significant advantages due to **low heat transfer of biomass**

Why Microwave? MW industrial application

- ✓ **Radar**
- ✓ **Special ceramic production**
- ✓ **Drying**
- ✓ **Food industry**
- ✓ **Polymerisation**
- ✓ **Chemical processing/synthesis**

CAPEX/OPEX Data- Sairem 915 MHz Continious processor

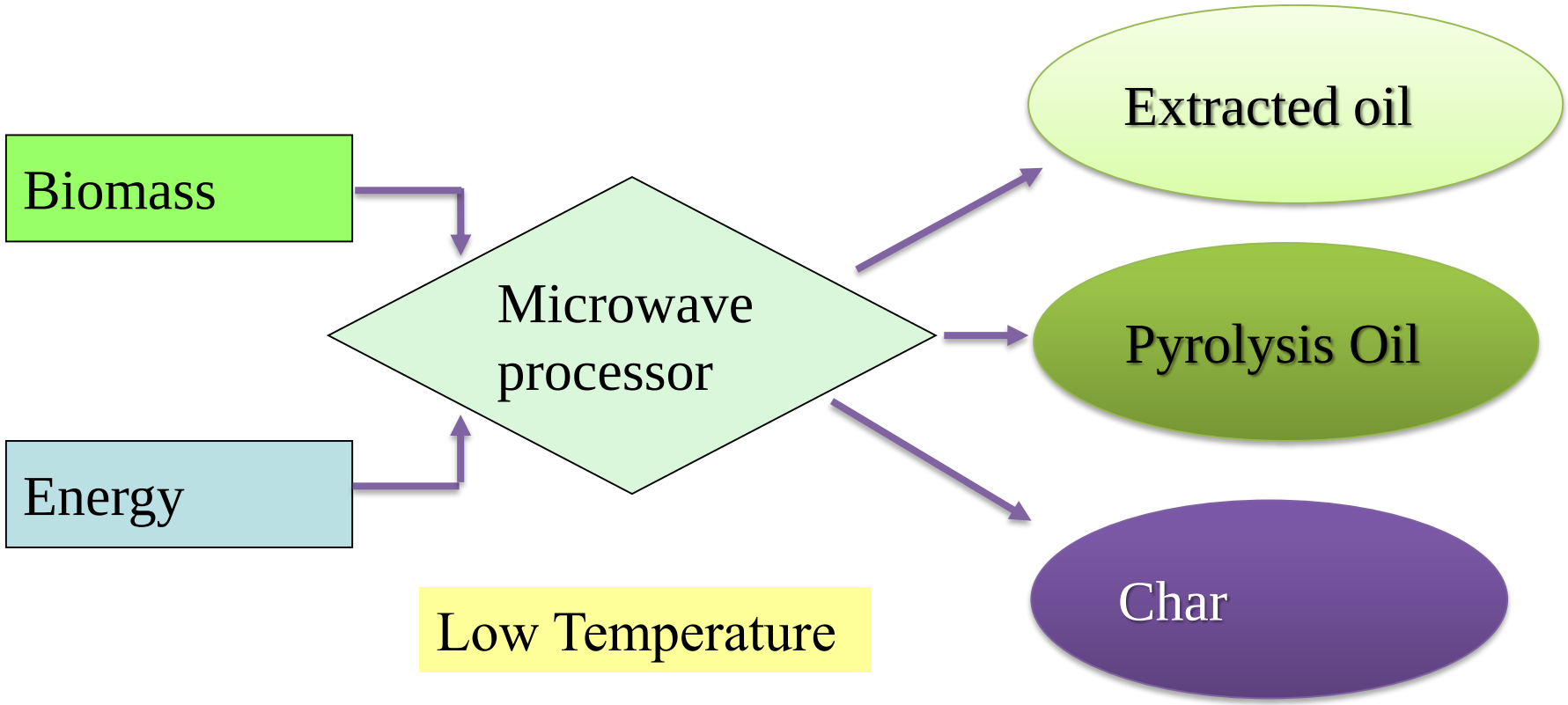
Version	Magnetrons	Capacity	Width (m)	Depth (m)	Height (m)	Cost (£)
TMW75	1 x 75kW	2.5 – 3 T/h	9	3	1.8	160,000*
TMW150	2 x 75kW	5 – 6 T/h	12	3	1.8	277,000*
TMW225	3 x 75kW	7.5 – 9 T/h	15	3	1.8	n/a
TMW300	4 x 75kW	10 – 12 T/h	18	3	1.8	485,000**

*Figures provided (originally in €)by Sairem in 2016
**Figure calculated from TMW75 and TMW150 cost

TMW75 Microwave Tunnel – used to defrost food -20°C to -2°C

Cost of 100 kW magnetrons is around 100k

Microwave Treatment of Biomass



Wide range of feedstock + Flexibility of Microwave Parameters (time, temperature, power) = Wide range of products

Budarin *et al.* The preparation of high-grade bio-oils through the controlled, low temperature microwave activation of wheat straw .BIORESOURCE TECHNOLOGY, **100** (23),pp: 6064-6068, 2009

Two main approaches of biomass activation

Pyrolysis

Microwave **treatment under inert atmosphere** (140 – 300 ˚C)

Key benefits:

- Applicable to all biomass
- Fast formation of biofuels : biogas, biochar and bio-oil
- *In-situ* fractionation results in low-acidity stable bio-naptha
- Can specifically target components of biomass

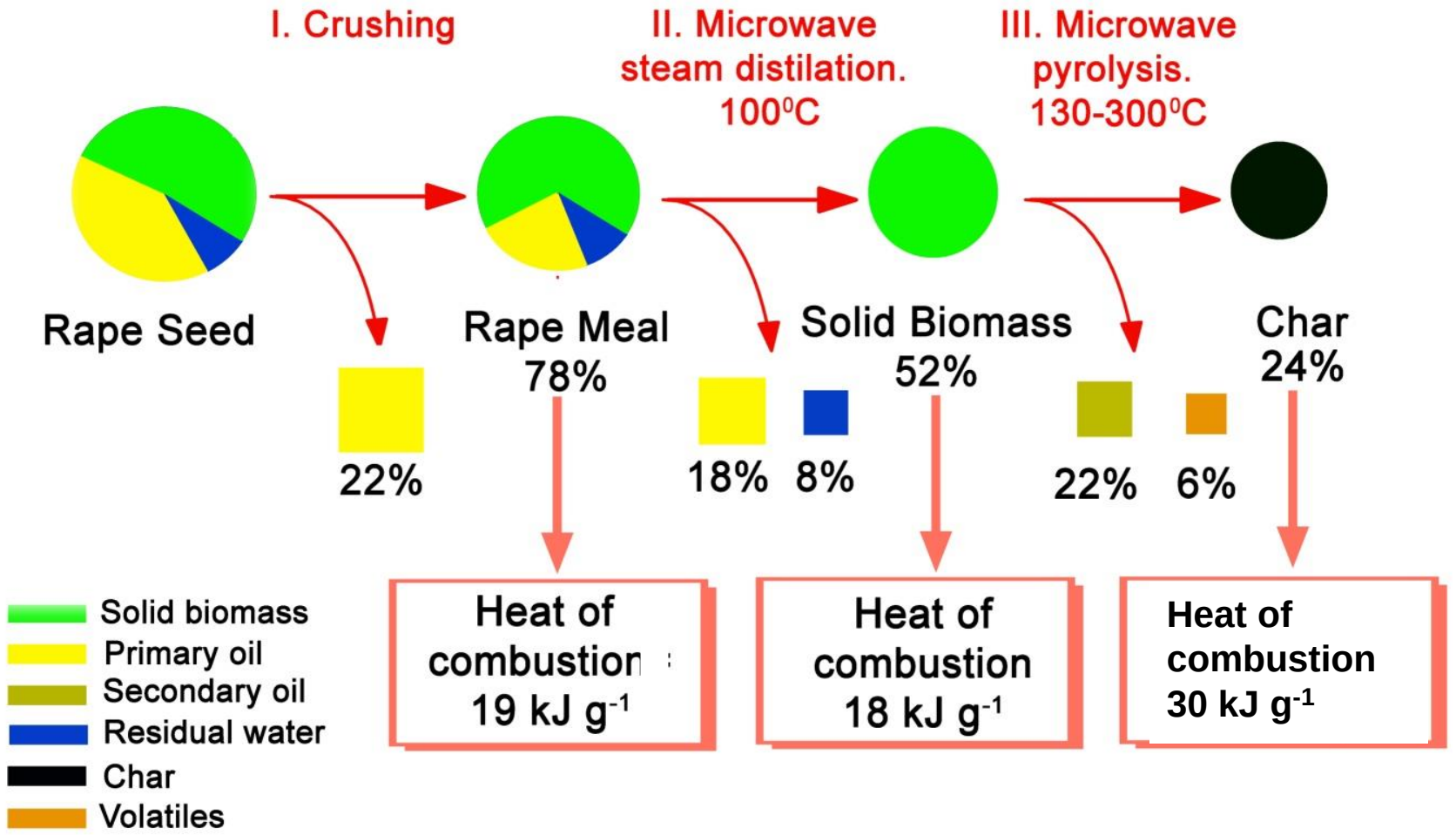
Hydrolysis

Microwave **treatment in water** (100 – 260 ˚C)

Key benefits:

- Suitable for wet biomass,
- Efficient hydrolysis of polysaccharides to produce fermentable sugars
- Extraction and gelation of polysaccharides (e.g. pectin)

Case Study 1: Rape Seed Meal Pyrolysis



Products:

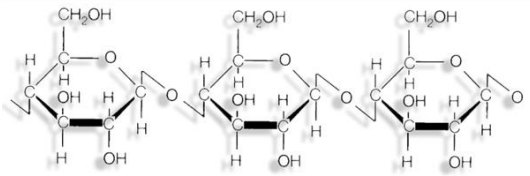
Primary oil: 40%; secondary oil: 22% ; char: 24 %; volatiles: 6 %; water: 8 %.

Investigated biomass

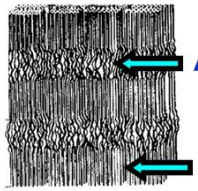
Model Compounds	Whole Biomass	
Cellulose	Soft Wood	Rape Straw
Hemi-cellulose	Hard Wood	Citrus waste
Lignin	Wheat Straw	Grass
	Oat straw	Seaweed
Maltodextrin	Barley Straw	Microalgae
Glucose	Barley Dust	Whisky production waste
Alginic Acid	Rape Straw	
Pectin	Cocoa husks	DDGS
		DRAFT
	Waste Paper	Bracken

Microwave activation of Biomass

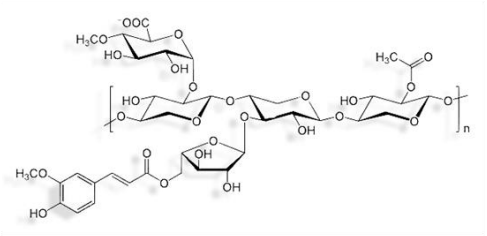
Cellulose



3-d Structure:

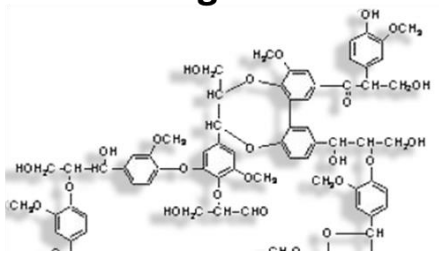


Hemicellulose



Unstructured

Lignin



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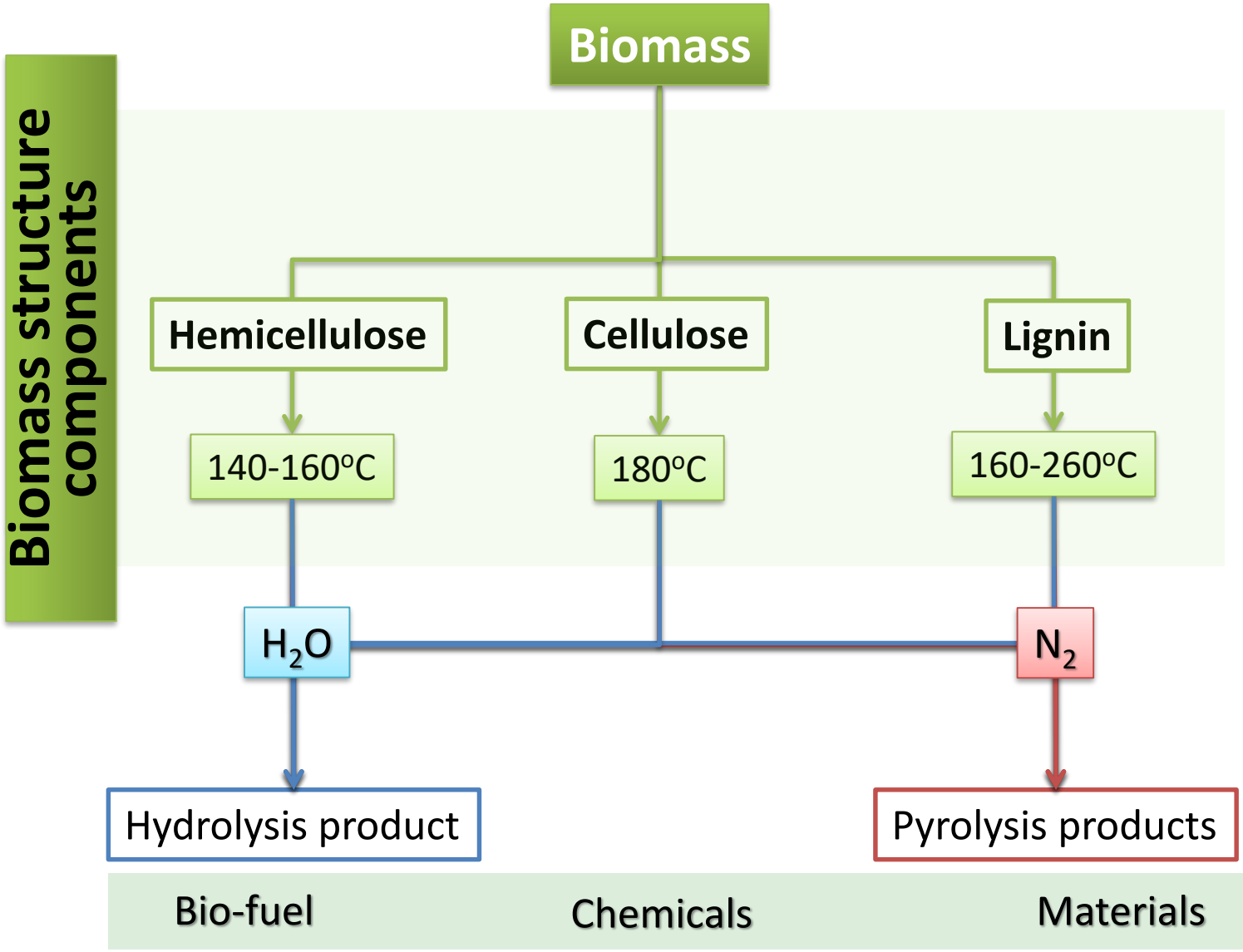
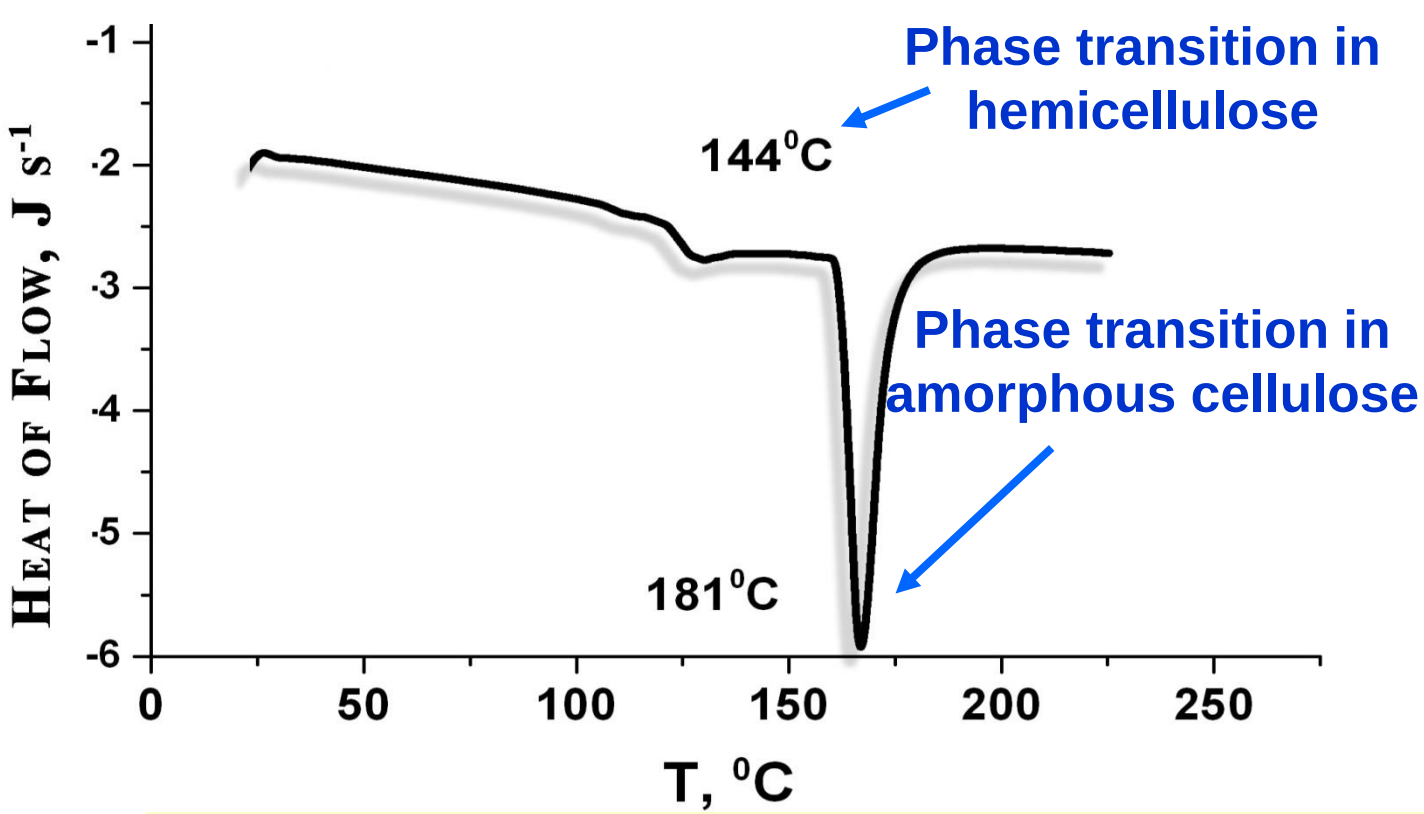


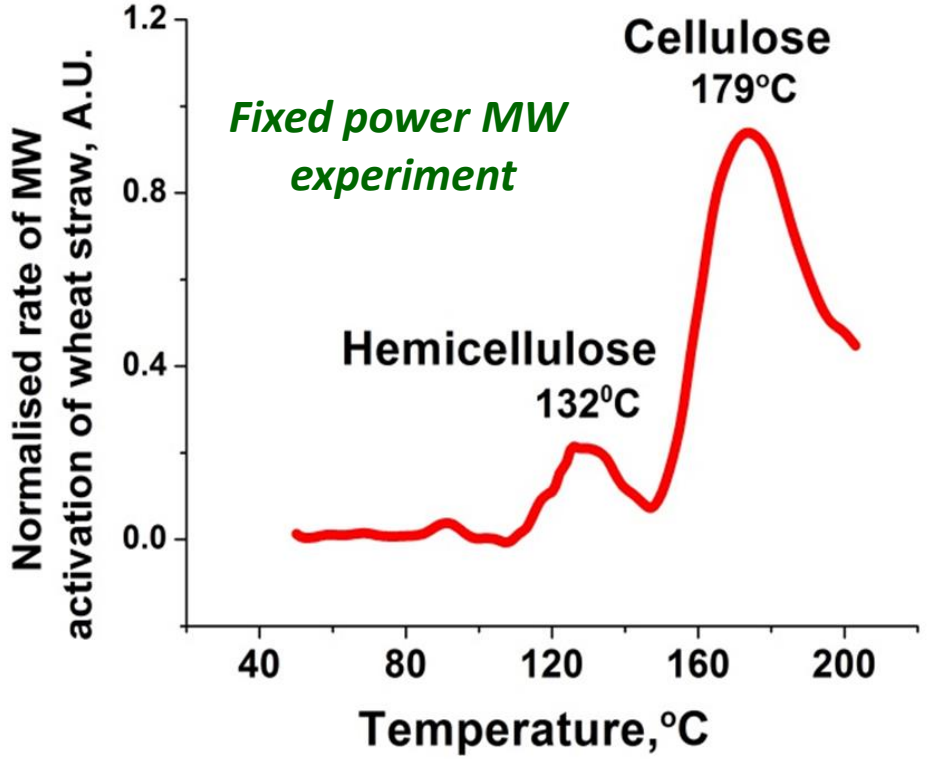
Budarin *et al.* Microwave assisted decomposition of cellulose: A new thermochemical route for biomass exploitation. BIORESOURCE TECHNOLOGY, **101** (10),pp: 3776-3779, 2010

Modulated DSC trace of pure cellulose

MDSC permits separation of the total heat flow signal into its thermodynamic (heat capacity) and kinetic components.

Heating rate is very informative parameter of MW pyrolysis





The phase transition points are an a good agreement with polymer decomposition temperatures

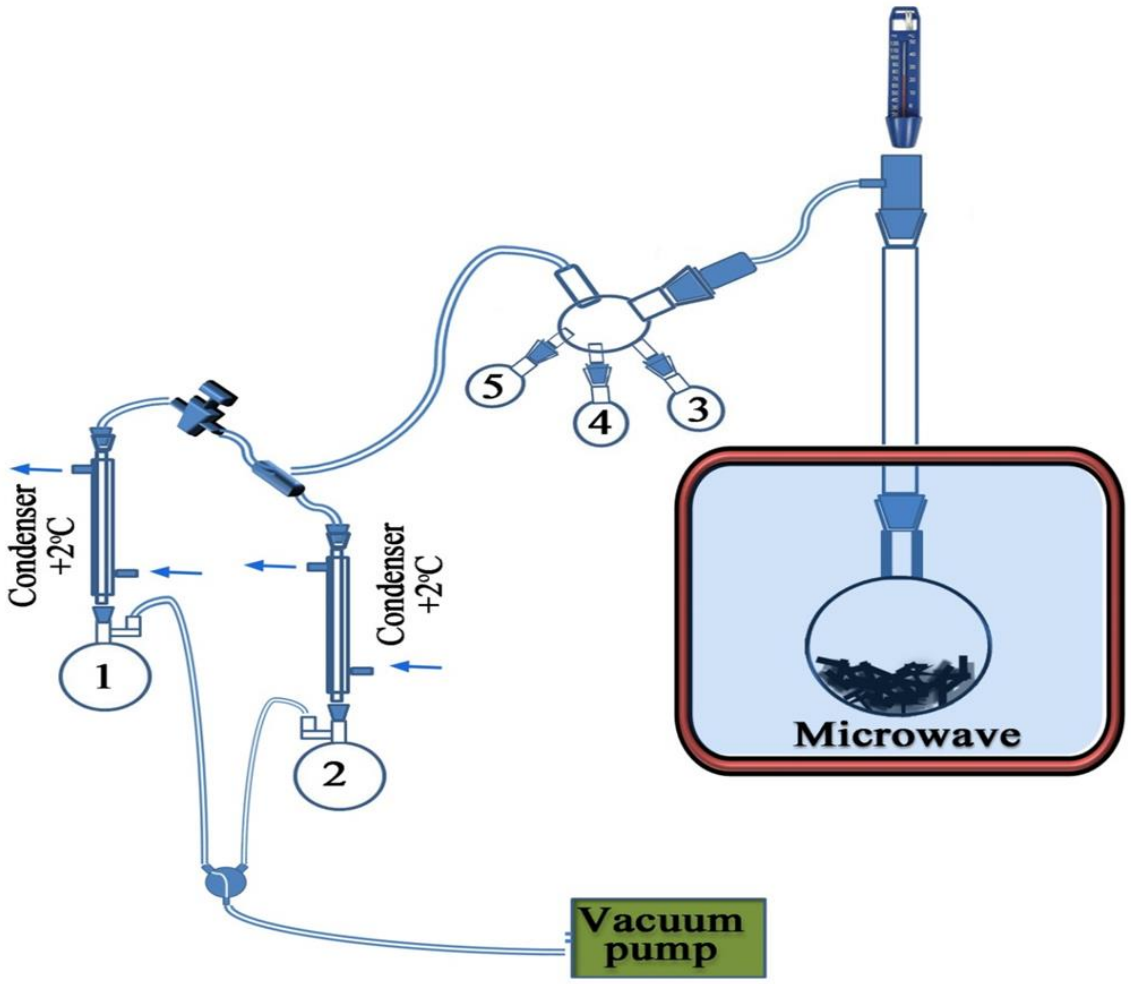
Budarin *et al.* Microwave assisted decomposition of cellulose: A new thermochemical route for biomass exploitation. BIORESOURCE TECHNOLOGY, **101** (10),pp: 3776-3779, 2010

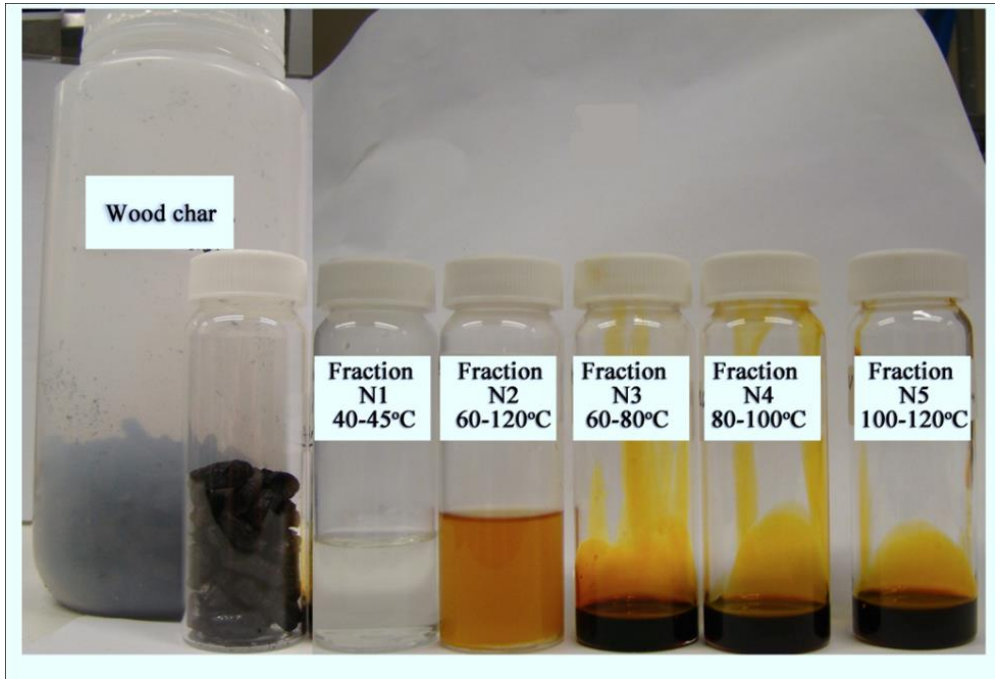
Characteristics of MW Bio-Char

- **High calorific value**
- **Good grindability**
- **Good hydrophobicity**
- **Co-firing with coal**

Masek, O *et al*. Microwave and slow pyrolysis biochar-Comparison of physical and functional properties , JOURNAL OF ANALYTICAL AND APPLIED PYROLYSIS, **100**, pp**:** 41-48, 2013

In-situ bio-oil separation





In-situ fractionation to valuable products:

- Fraction 1 physisorbed water
- Fraction 2 (acid, water) source of acids for bio-surfactants
- Fraction 4 (sugars) basis for platform molecules
- Fractions 3 & 5 (Phenols, furans) drop-in replacements for petrochemical industry

Comparison microwave oil characteristics with competitors (saw dust).

Property	Crude Oil[1]	Pyrolysis oil	Microwave oil	
			Ruan[2]	Current York
Water (%)	<1	**10-20**	15.2	**<1**
C (wt %)	85-87	45-55	60.1	58.9
H (wt %)	10-14	6-7	7.70	6.85
N (wt %)	0.1-2	0.3	2.02	1.15
S (wt%)	0	0.5-5	0.15	0.02
Acid number	<1	**70-150**	pH= 2.87	**1.4** (pH=7)
Alkali metal	**50**	100	7.6	**6**
CV (kJ/g)	42	**16 - 21**	17.4	**16-22**

1.Low water content
2.Low acid content.
3.Low alkali metals content.
4.The high yields of fermentable sugars:
- Levoglucosan (up to 50%)
- Levoglucosanone (up to 25%)

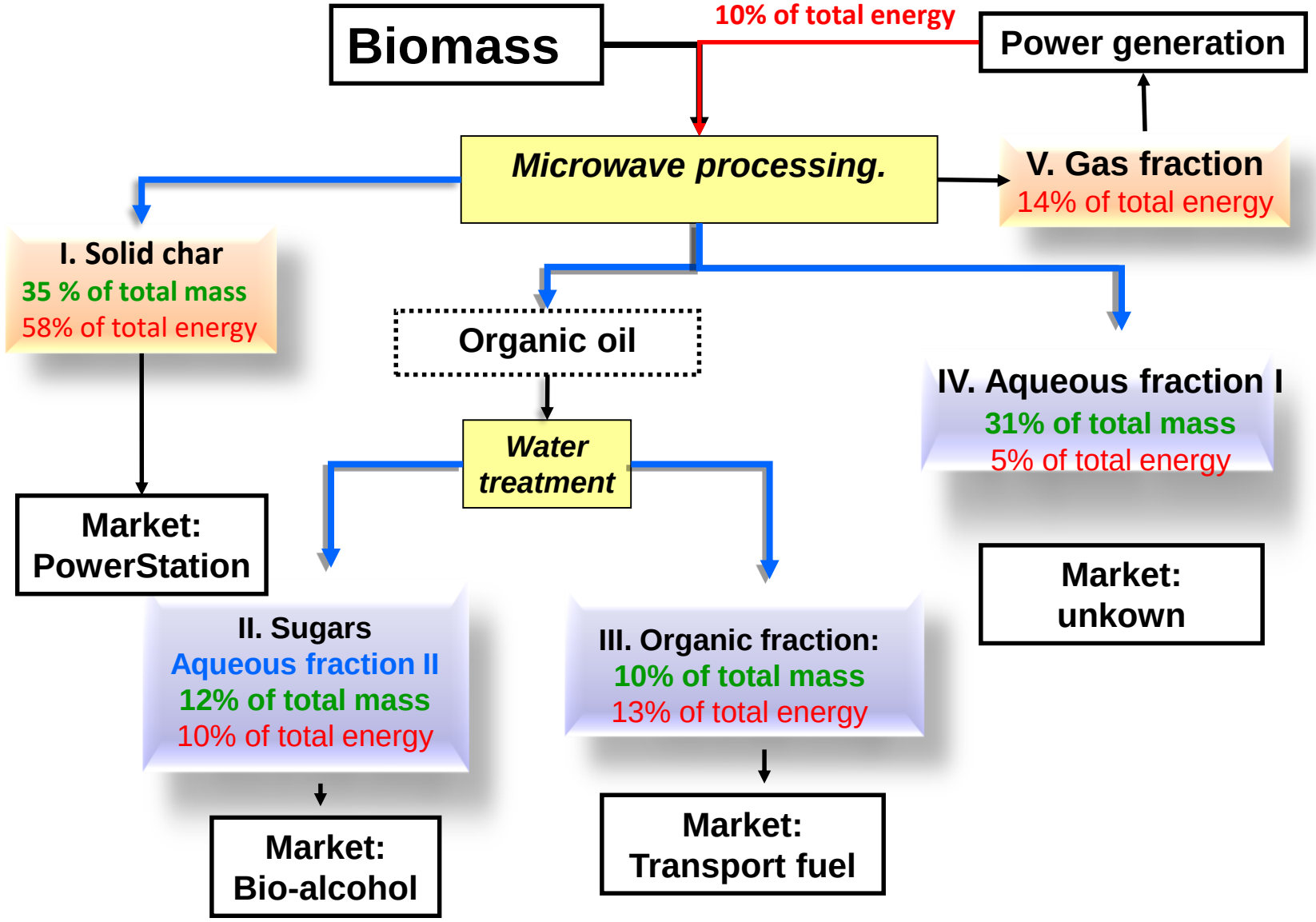
[1] Report 40661. The Exploitation of Pyrolysis Oil in the Refinery Main Report. Prepared For: The Carbon Trust. March 2008.
[2] Yu F., Deng S., Chen P, LIU Y., Wan Y., Olson A., Kittelson D., and Ruan R. "Physical and Chemical Properties of Bio-Oils. From Microwave Pyrolysis of Corn Stover", *Applied Biochemistry and Biotechnology*, 2007, **136–140**, pp 957-950.

Bio-Oil Yield

Sample	York Microwave Pyrolysis Products Yield (%)				Flash pyrolysis Liquid yield (%)
	Bio-Char	Aqueous	Bio-Oil	Liquid[a]	
Bracken	47.9	15.3	22.8	38.1	-
Wheat Straw	39.4	22.2	26.1	**48.3**	**47.1**
Paper	41.5	17.6	23.4	**42.2**	**49.1**
Wood	26	41	19	**60**	**62.0**
Barley Dust	45.7	15.9	18.9	34.8	-
Reed Canary Grass	45.6	15.9	23.0	**38.9**	**44.0**

[a] Aqueous + Bio-oil

Case Study 2: Microwave-assisted wheat straw biorefinery



Budarin *et al.* "Use of green chemical technologies in an integrated biorefinery". *Energy & Environmental Science* (2011), **4**(2) 471-479.

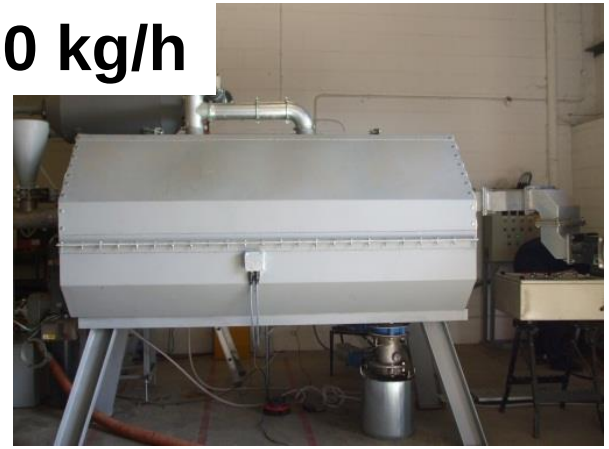
Wheat straw pyrolysis. Energy Impute. Comparison of alternative methods of estimation

Theoretical calculation	1.36 kJ/g
Experimental. Small scale extrapolation	1.5 kJ/g
Experimental. Large scale	1.7 kJ/g

Budarin *at al.* "Use of green chemical technologies in an integrated biorefinery". *Energy & Environmental Science* (2011), **4**(2) 471-479.

Microwave-assisted wheat straw biorefinery
Semi-scale trial

Microwave processor . 30 kg/h



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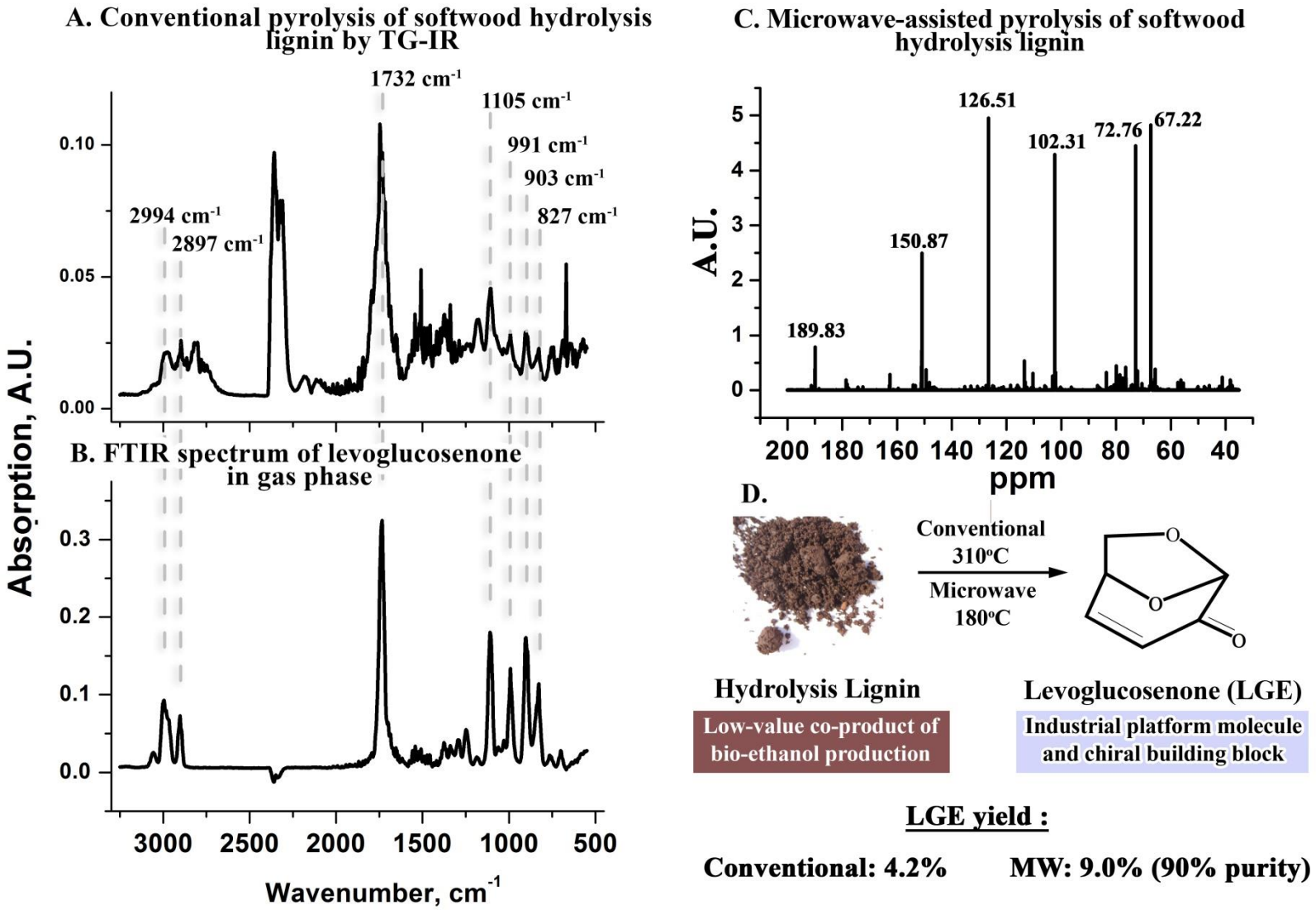
18 kg of wheat straw = **6.7 kg of char** **+** **5.7 of oil**

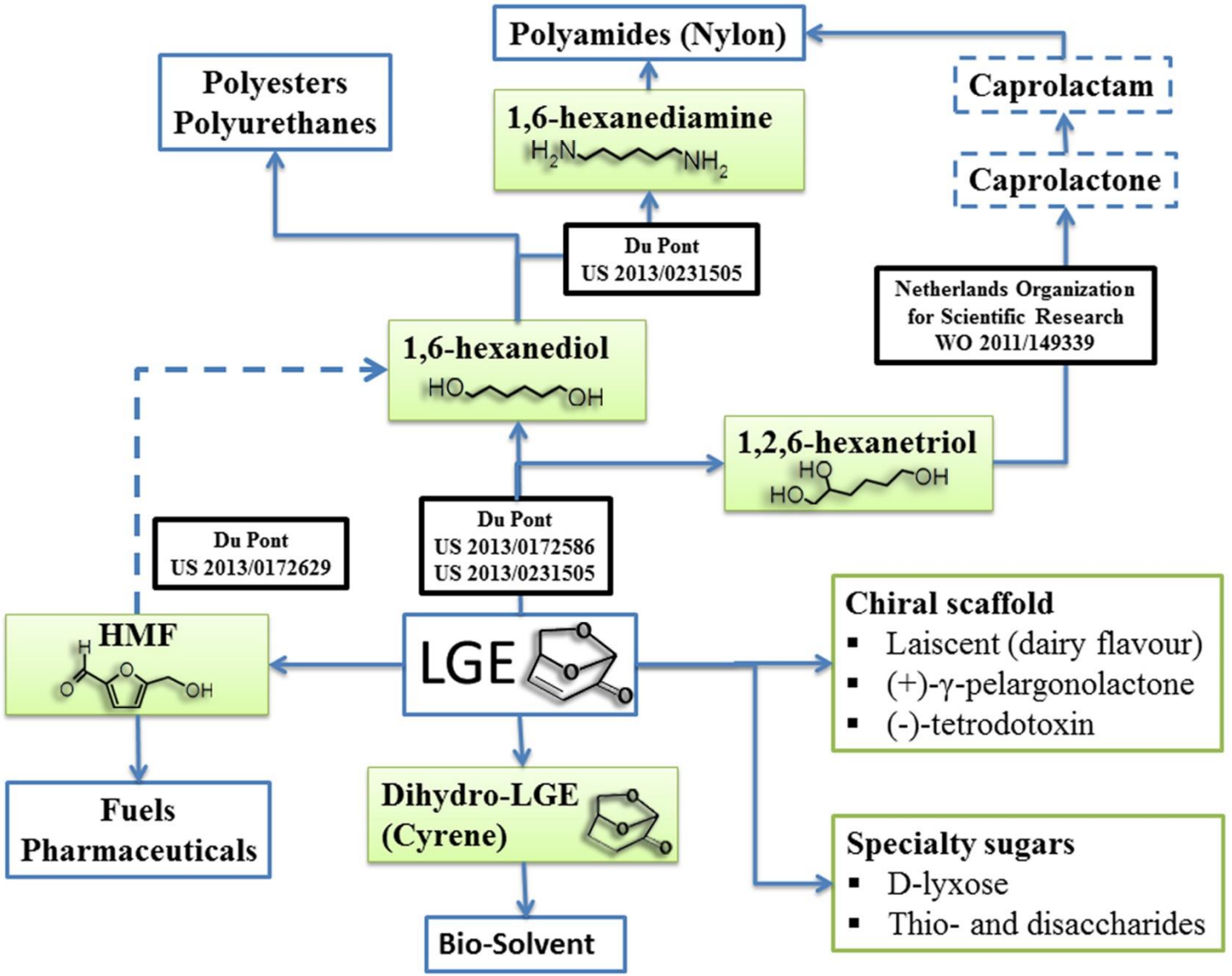
Case Study 3:Microwave activation of hydrolysis lignin.



Levoglucosenone is produced from saccharide part of Lignin

De Bruyn *et al*. A new perspective in bio-refining: levoglucosenone, ENERGY & ENVIRONMENTAL SCIENCE **9**(8), pp 2571-2574,2016

Levoglucosenone applications



De Bruyn *et al*. A new perspective in bio-refining: levoglucosenone, ENERGY & ENVIRONMENTAL SCIENCE **9**(8), pp 2571-2574,2016

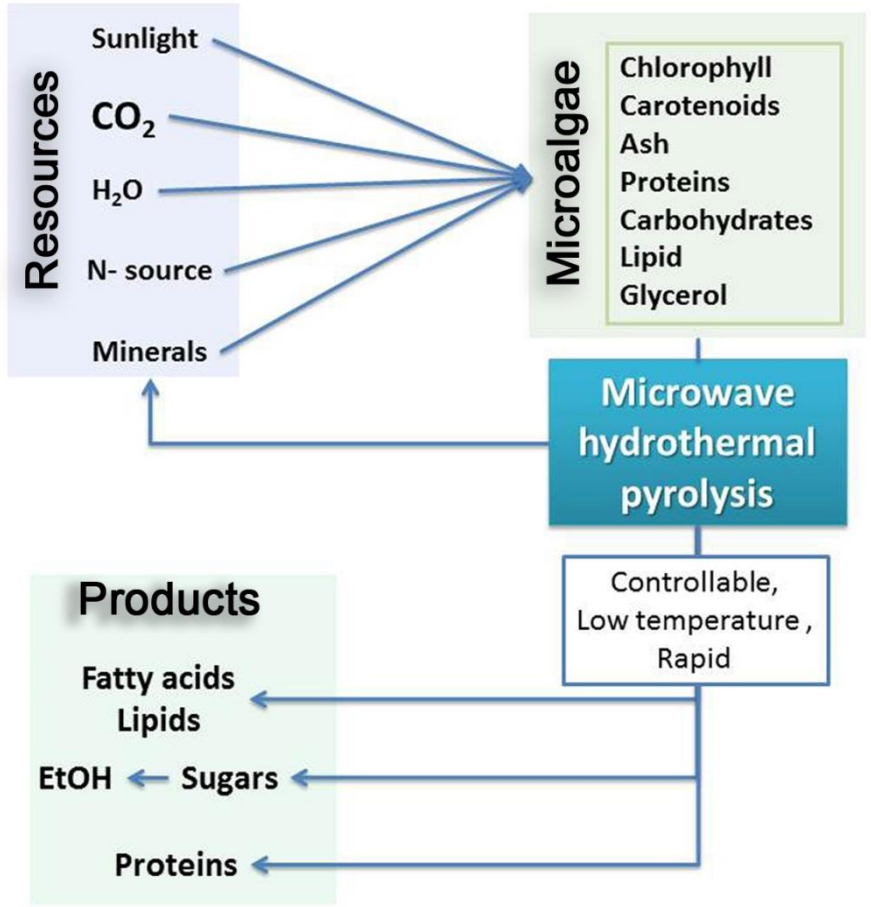
Hydrothermal MW-assisted activation of bio-mass

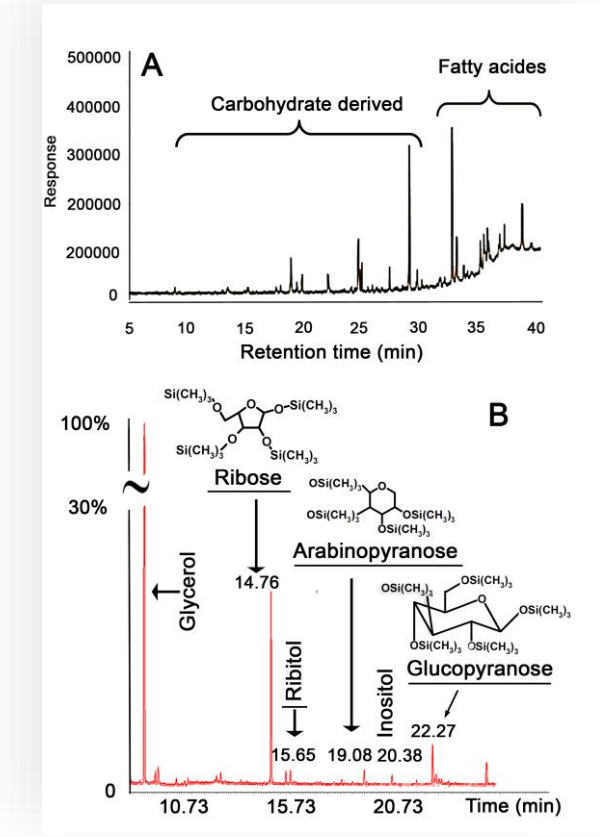
	Application
1	Hydrolysis of lignocellulosic biomass to fermentable sugars
2	Extraction of pectin from citrus peal
3	Microalgae biorefinery
4	Biomass pre-treatment before AD
5	Waste paper utilisation
6	Extraction high value chemicals from plants

Benefit of Microwave Hydrolysis

- ✓ **High efficiency of heating: water is the best microwave absorber**
- ✓ **Saving energy of water vaporisation**
- ✓ **Direct solubilisation of biomass due to hydrolyses of polysaccharides**

Case Study 4: Microalgae biorefinery

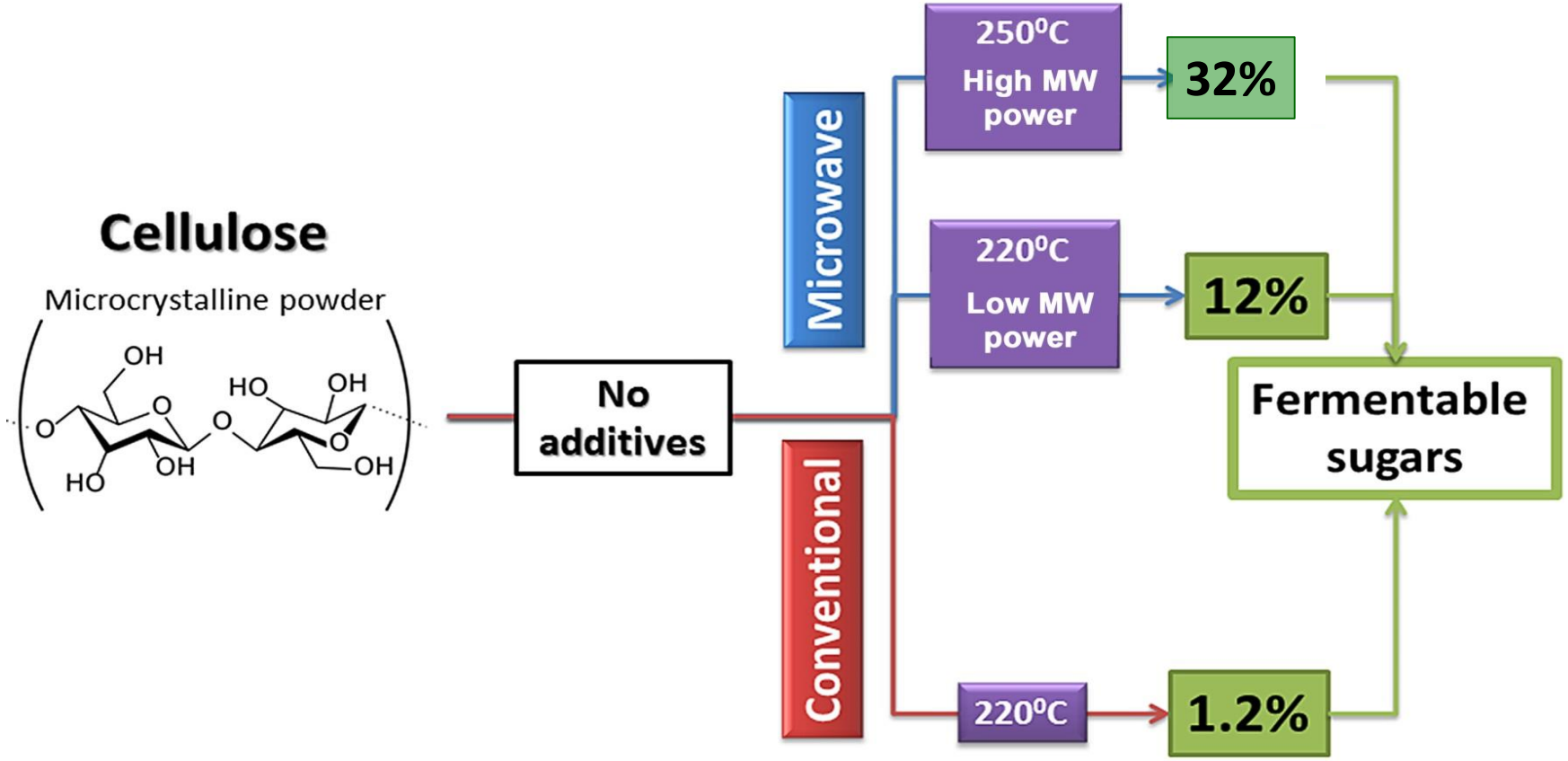




- **Up to 80% of Microalgae was transformed to valuable products**

Budarin at al., Microalgae biorefinery concept based on hydrothermal microwave pyrolysis. GREEN CHEMISTRY (2012) **14** (12) 3251-3254

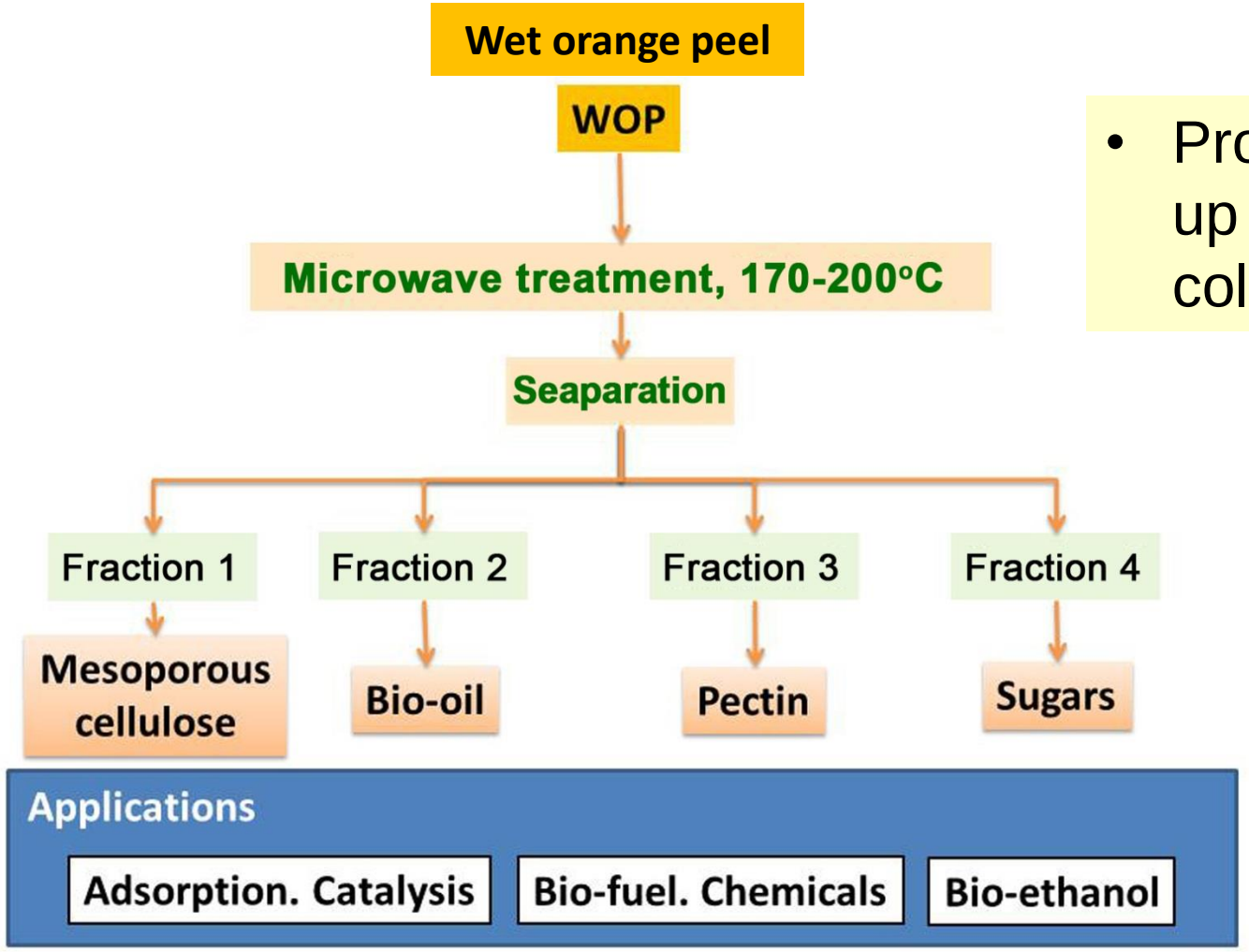
Case Study 5. Cellulose Hydrolysis



- **Sugars yield increases x20 in the presence of microwave irradiation**
- **High selectivity toward glucose. Repeated MW hydrolysis of solid produces up to 40% yield of sugars at 220°C**

Fan et al, *JACS*, 2013, 1178 Chemical Engineering and Processing, 2013

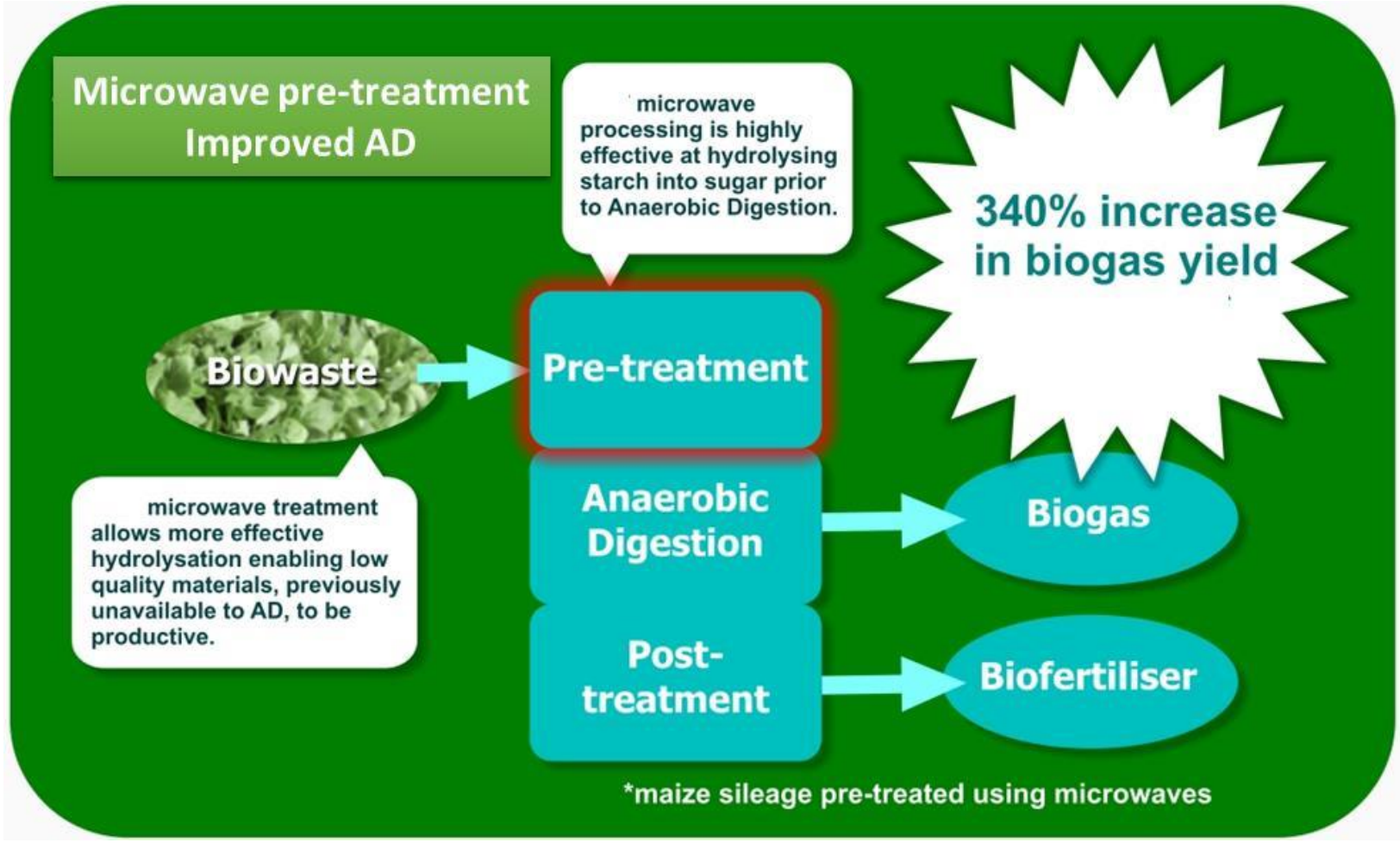
Case study 6. MW bio-refinery of Orange peel. Hydrothermal treatment



- Process being scaled-up with industrial collaboration

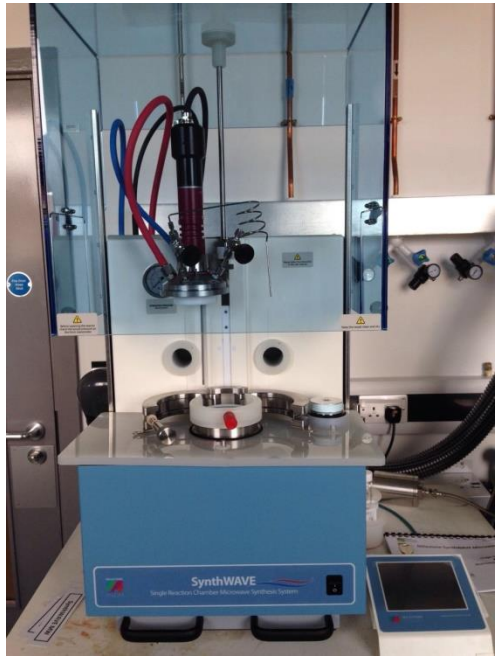
Balu A.M. et al. Valorisation of Orange Peel Residues: Waste to Biochemicals and Nanoporous Materials, **CHEMSUSCHEM**, **5(**9),pp: 1694-1697, 2012

Preliminary results: Microwave-improved anaerobic digestion.

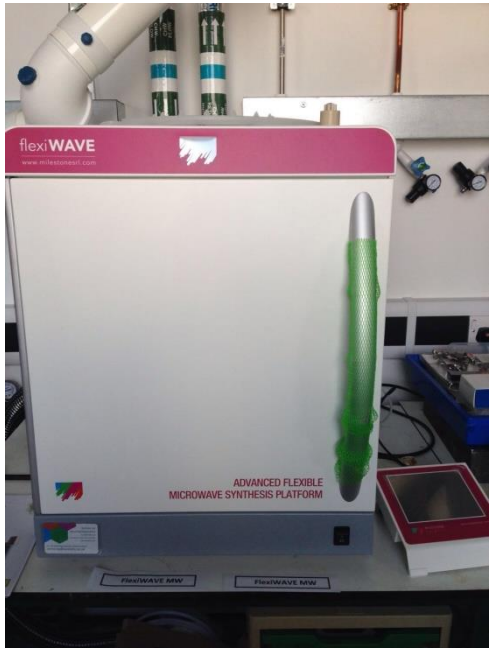


New MW Equipment

synthWAVE microwave



flexiWAVE microwave



HPLC

Large microwave facilities at York

Continuous microwave pyrolyser.
30 kg/h
6 kW, 100-200^{o}C

Continuous microwave hydrolyser. 20L
Semi-continuous, 60-180^{o}C, 6kW

Industrial application of Microwave

- Clark DE, Sutton WH (1996) Microwave processing of materials. Annual Review of Materials Science, 26, 299–331.
- Industrial Microwave Heating, Volume 1, 1983, A. C. Metaxas, Roger J. Meredith, Publisher IET, 1983, 357 pages. ISBN 0906048893
- Kitchen, H.J., Vallance, S.K., Kennedy, J.L., Tapia-Ruiz, N. , Carassiti, L., Harrison, A., Whittaker, A.G., Drysdale, T.D., Kingman, S.W., Gregory, D.H. "Modern Microwave Methods in Solid-State Inorganic Materials Chemistry: From Fundamentals to Manufacturing" *Chemical Reviews*, 2014,114 (2), 1170-1206; DOI: 10.1021/cr4002353
- Thermex Thermatron, LP http://www.thermex-thermatron.com/
- Leonelli, C. & Mason, T. J. Microwave and ultrasonic processing: Now a realistic option for industry. *Chemical Engineering and Processing* **49**, 885-900, doi:10.1016/j.cep.2010.05.006 (2010).
- Introduction to Food Engineering (Fifth Edition) R. Paul Singh and Dennis R. Heldman (ISBN-13: 9780123985309), Series: Food Science and Technology, Publisher: Elsevier Science Publishing Co Inc, Academic Press Inc, 2013, pages: 892
- http://nifa.usda.gov/blog/microwave-pasteurization-new-industrial-process-producing-high-quality-and-safe-food
- http://www.microdenshi.co.jp/en/applied/rubber/1.html
- K. T. Higgins, *Food Progressing, http://www.foodprocessing.com/articles/2015/industrial-microwave-technology/*, 2015.
- *Microwave Assisted Processing, Radient,http://www.radientinc.com/*.
- *Advanced Microwave technologies, http://www.advancedmicrowavetechnologies.com/*, 2010.

Thank you !