THE UNIVERSITY of York

Towards a wheat straw based biorefinery

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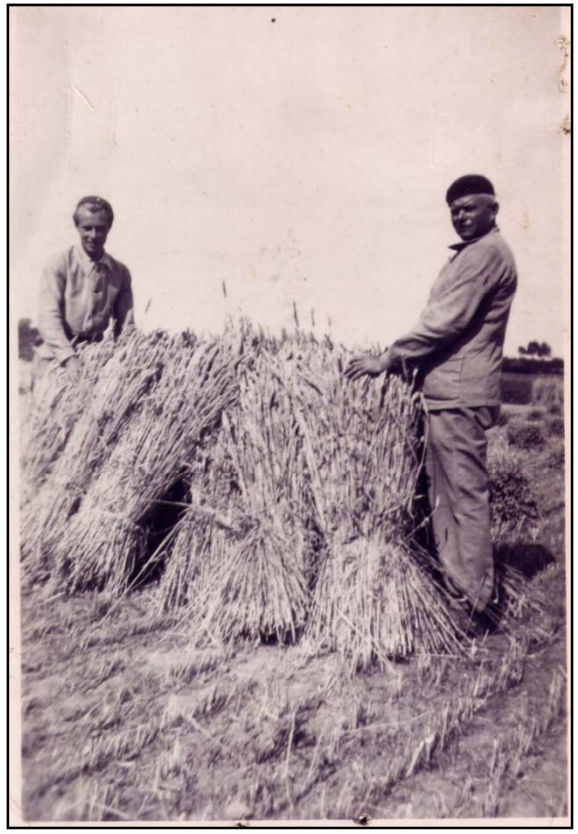
Green Chemistry
Centre of Excellence

PLAN

- Background to the project
- Supercritical CO_2 extraction
  - Pilot-scale
  - Small production-scale
- Supercritical CO_2 fractionation
- Uses for the lignocellulosic fraction
- Density issue
- Wheat straw biorefinery
- Conclusions and future work

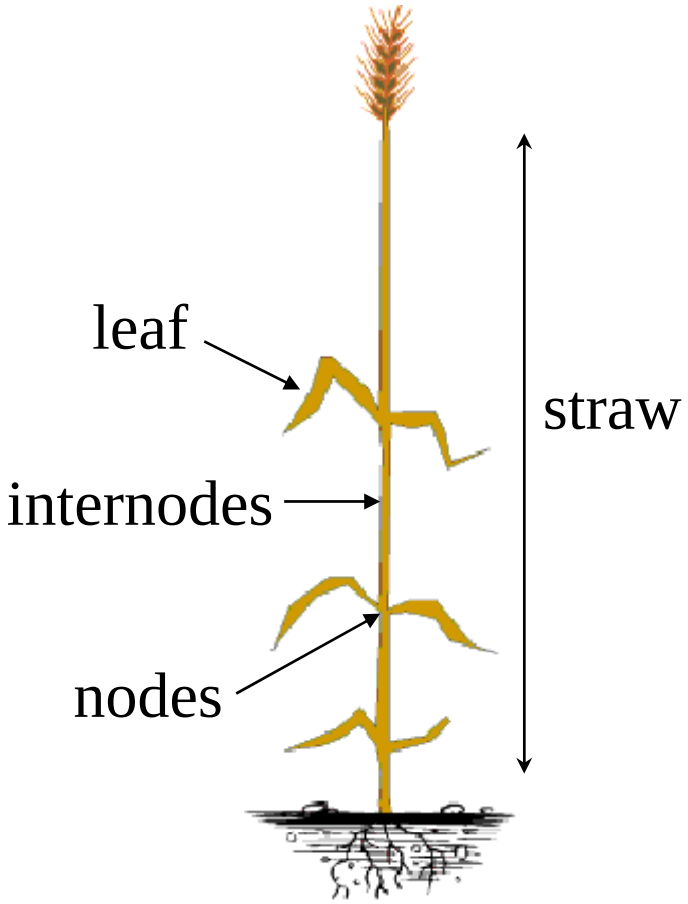


WHAT IS WHEAT STRAW ?

- Wheat - one of the largest crop species in the world

- Straw - stem from which the seed head has been removed

  - 3 botanical components
  - surplus: | UK 4MT
    | EU-25 108MT



TRADITIONAL USES

Burning

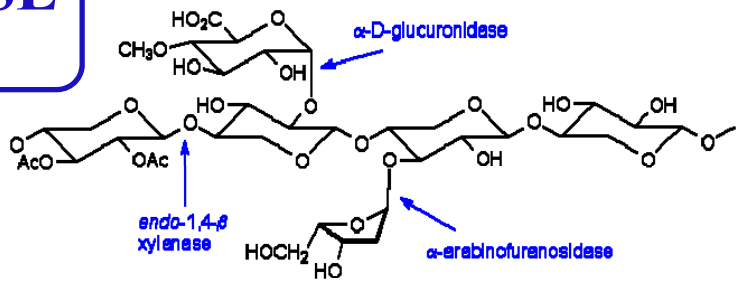
WHEAT STRAW

Incorporation

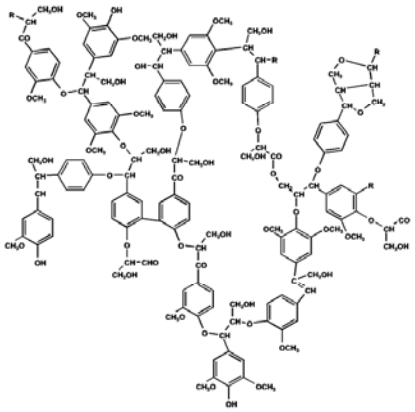
Feeding/Bedding

CHEMICAL COMPOSITION

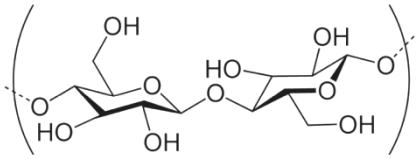
HEMICELLULOSE
(25-35%)



LIGNIN
(15-20%)

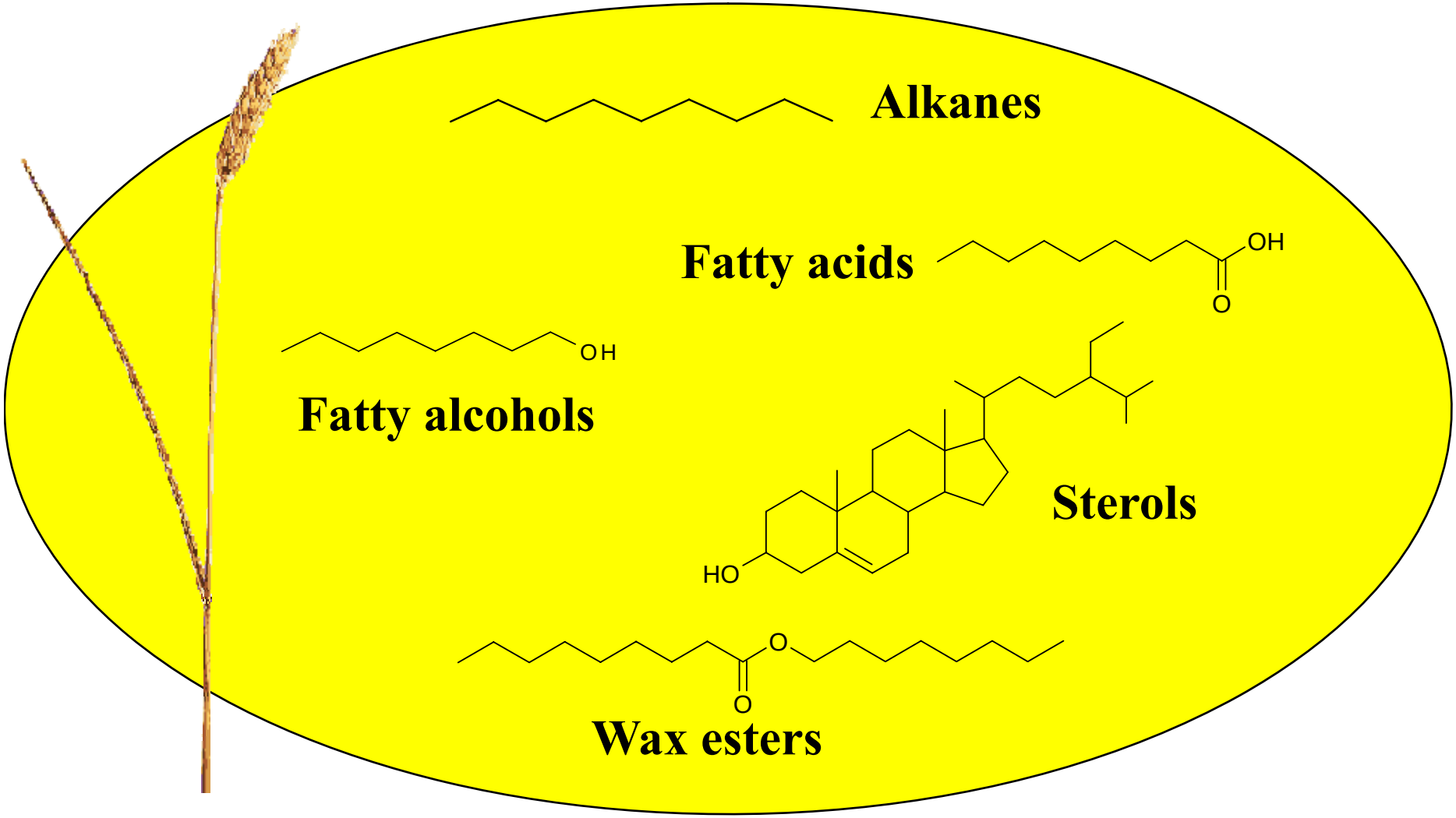


CELLULOSE
(45-55%)



MINOR CONSTITUENTS
(5-10%)

WHEAT STRAW WAXES



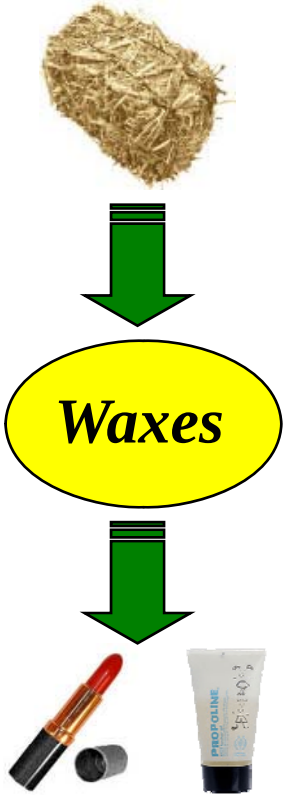
APPLICATIONS

📖 ***http://www.bbsrc.ac.uk/science/initiatives/CIMNFC3.pdf***

- 92 per cent of women in industrialised countries use lipstick.
- 'Miss Average' will put on around 3kg of lipstick on her lips throughout her lifetime.

📖 ***G. Frobose and R. Frobose, Lust and Love - Is it more than chemistry?, RSC, London, 2006***

• **STRAWFRAC -** Value Added Products from Wheat Straw



COSMETICS, COATINGS, ETC..

TRADITIONAL SOLVENT EXTRACTION

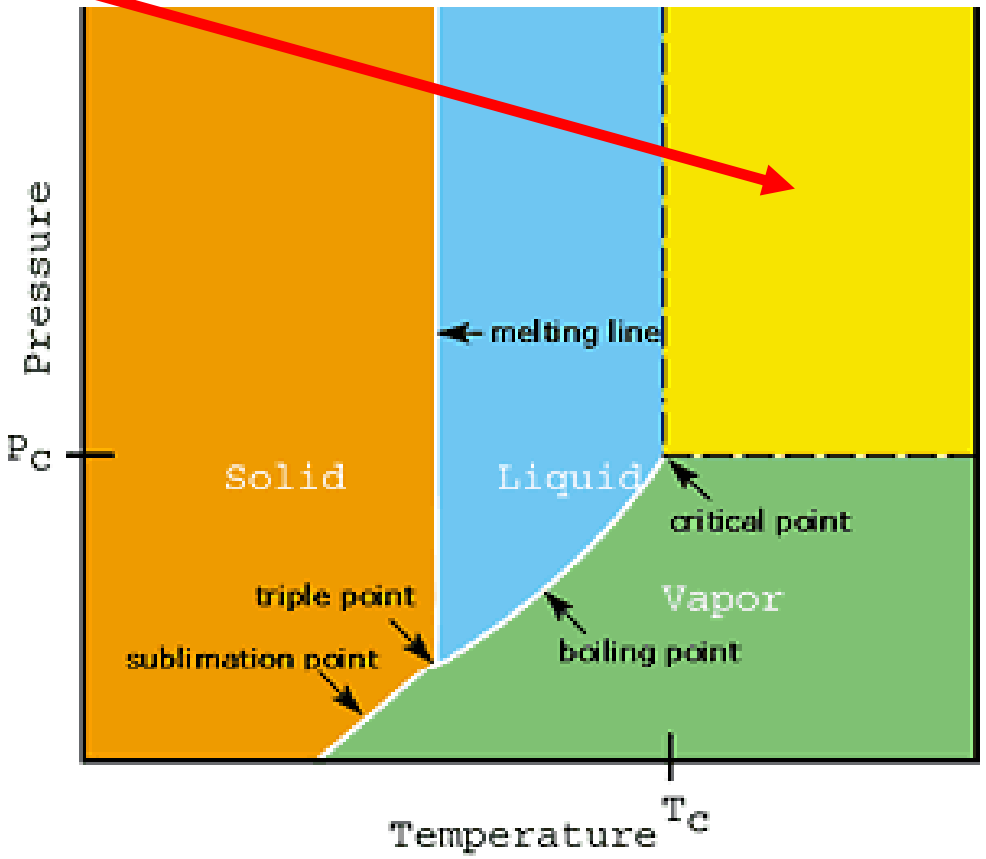
CHEAP but:

- Unselective technique
- Energy-intensive solvent evaporation
- Wasteful purification steps
- Use of toxic solvents (e.g. chloroform, benzene, hexane..)

SUPERCRITICAL CO_2 EXTRACTION

SUPERCRITICAL FLUID = substance above both its critical T(T_C) and P (P_C)

CO_2	Tc = 31 °C Pc = 73 bars



SUPERCRITICAL CO_2 EXTRACTION

Advantages:

- Cheap & widely available
- Safe – non toxic or flammable
- Avoid use of VOCs
- Solvent power can be tuned by simply changing P and T
  - extremely selective technique
  - stage-wise fractionation
- Low viscosity aids rapid extraction
- Leaves no solvent residues
- Can be easily recycled

$ScCO_2$ extractor used for decaffeinating coffee

📖 ***http://www.natex.at/index.html***

SUPERCRITICAL CO_2 EXTRACTION

Drawbacks:

- High capital installation costs
- Relatively high running costs
- Requires technically skilled operators

Green but expensive technology

Only economically viable for high value extracts!

$ScCO_2$ extractor used for decaffeinating coffee

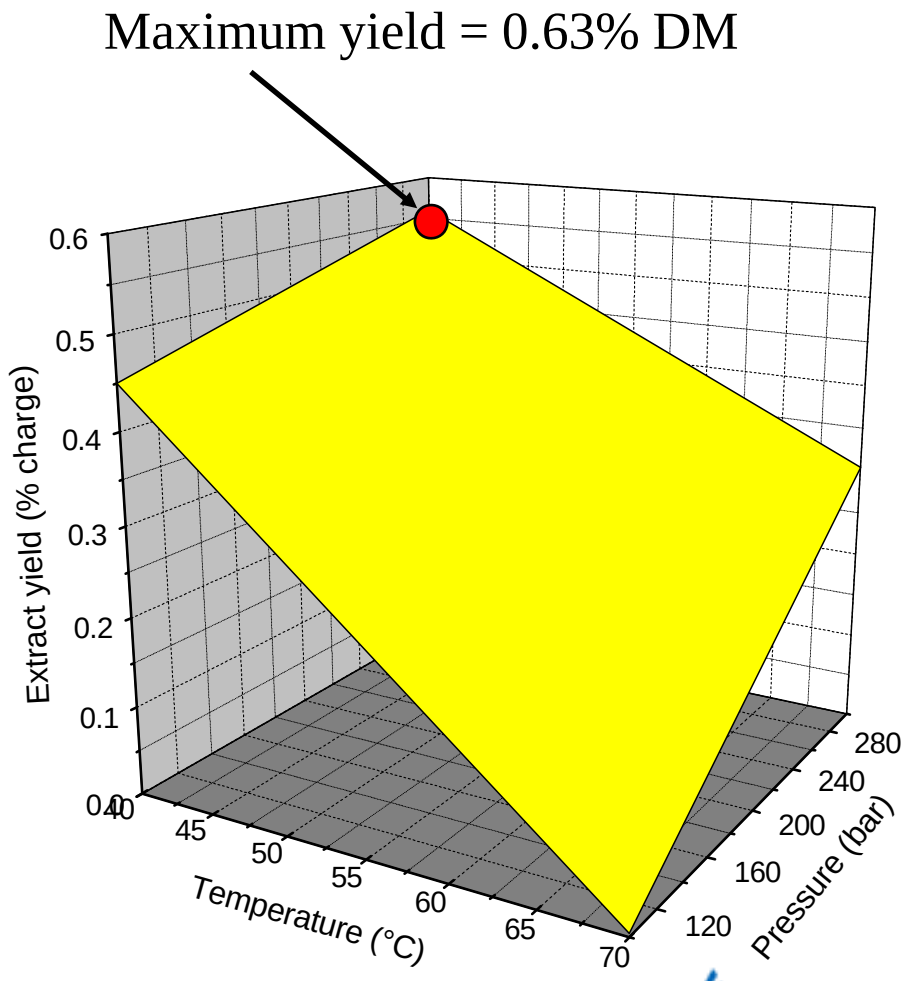
📖 ***http://www.natex.at/index.html***

PILOT SCALE EXTRACTION

- Wheat variety – Sabre
- Scale – 200 g
- 2^2 factorial design

Optimal conditions

- 40ºC
- 300 bar
- 40 min



📖 *F. E. I. Deswarte, J. H. Clark, J. J. E. Hardy, P. M. Rose, Green Chem., 2006, 8, 39-42.*

BOTANIX

PRODUCTION SCALE EXTRACTION

Adoption of the optimal operating conditions determined at pilot scale

ground wheat straw
74.19 kg

Production-scale supercritical CO2 extractor

wheat straw waxes
770.6 g

PRODUCT TESTING

	Pilot scale	*Production scale*
Variety	***Sabre***	***Sabre***
Harvest year	***2003***	***2005***
Wax content (%DM)	***0.90 ± 0.06***	***0.81 ± 0.01***
Extraction yield (% DM)	***0.55***	***1.04***

-11%

× 2

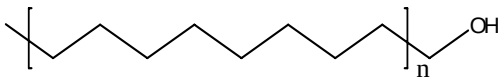
HIGH VALUE WAX FRACTIONS (1)

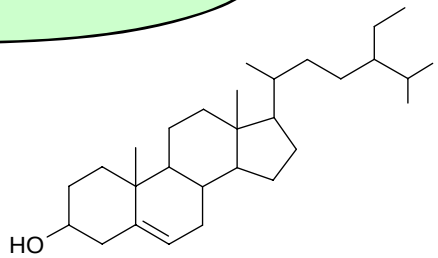
Waxes

COSMETICS, COATINGS, ETC..

Polycosanols

Sterols





CHOLESTEROL REDUCING AGENTS

📖 *I. Gouni-Berthold, H. K. Berthold, Am. Heart J., 2002, 143, 356-365.*

📖 *V. Piironen et al., J. Sci. Food Agric., 2000, 80, 939-966.*

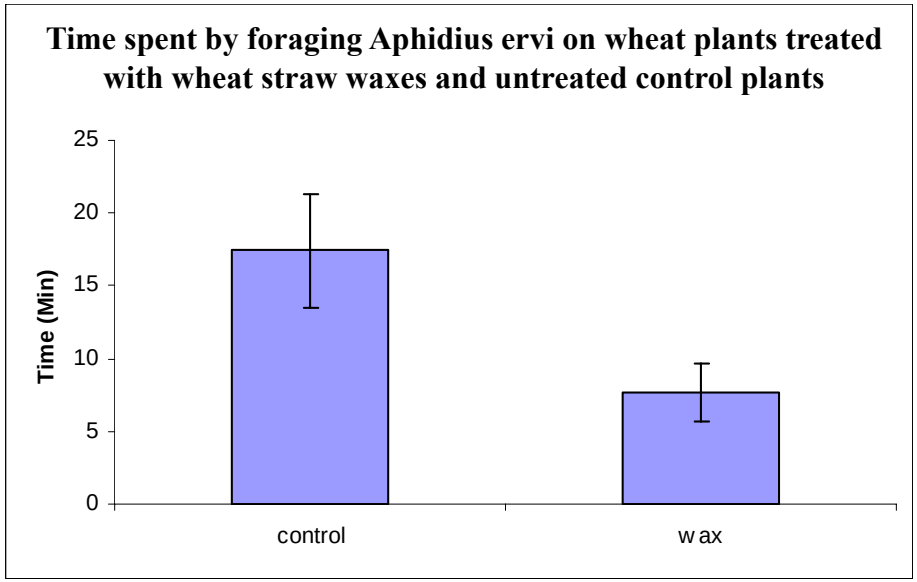
HIGH VALUE WAX FRACTIONS (2)

INSECT SEMIOCHEMICAL

- Lady bird - natural ennemy of aphids
- Predation minimised through parasitoid avoidance of ladybird-inhabited plant surface
- wheat straw wax comprised a similar blend of compounds found in ladybird footprints.

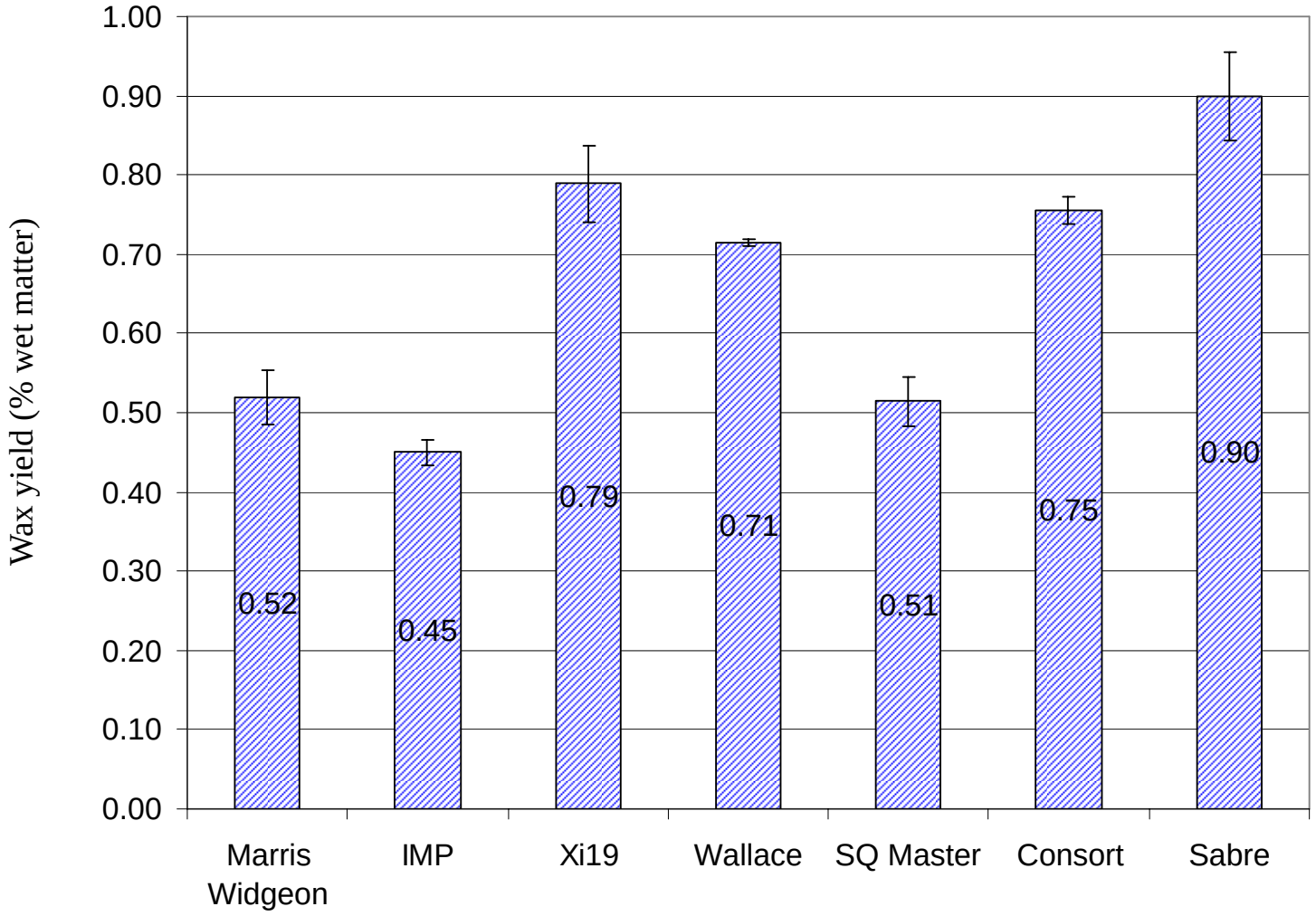
alternative to the use of broad spectrum pesticides

ROTHAMSTED RESEARCH



WAX YIELD - Δ BETWEEN VARIETIES

Varieties grown under field controlled conditions by Central Science Laboratory



LIGNOCELLULOSE -ENERGY

- Can be employed in dedicated straw-burning plants (e.g. Ely Power Station)
- Can be used cost effectively in co-firing plants

Straw pellets

www.draxpower.com

- Removal of wax had no appreciable effect on calorific value
- Co-extraction of large amounts of water is likely to positively affect calorific value and economics

Charles Jackson & Co Ltd

LIGNOCELLULOSE - PULP & PAPER

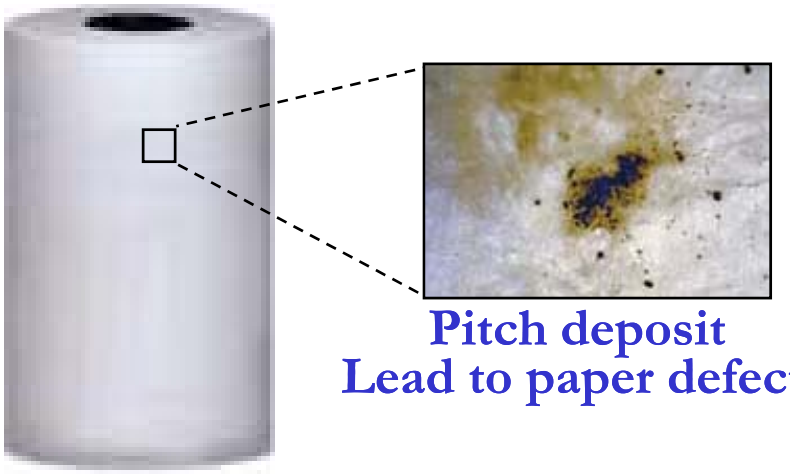
• Waxes are the source of many problems during pulp production

• Economic losses associated with pitch problems in pulp mills often amount to **1% of sales**

- pulp contamination
- shutdown of operation
- pitch control additives cost

Removing the wax adds value to the lignocellulosic fraction!

📖 *A. Gutiérrez et al., Trends Biotechnol., 2001, 19, 340-348.*



Pitch deposit
Lead to paper defects

• Removal of waxes could:

- eliminate pitch problems
- facilitate the penetration of pulping chemicals into straw

LIGNOCELLULOSE - STRAWBOARD

- Waxes are believed to interfere with the adhesion between straw particles and water-based binders
- Many destructive treatments have been described in the literature to improve bondability

📖 ***Marlit Ltd, WO Pat, 9 738 833, 2001***

Wax removal presents the added benefit of adding value to the fibre, which can then be processed using alternative, lower cost resins.

LIGNOCELLULOSE - GARDEN MULCH

Dewaxed VS. native
(wheat straw)

- Composting, stabilisation and plant germination were not affected

- Wax extraction could potentially assist with the Strulch patented process:

  - improve straw wettability and enhance uniformity of iron penetration.

  - since waxes generate phytotoxic hydrocarbons during decomposition, the maturation period may also be shortened.

Strulch®
www.strulch.co.uk

DENSITY ISSUE

~ 100 kg of loose straw

ρ × 10

grinding

~ 100 kg of ground straw

Key issues associated with the low density of wheat straw:

- Transport
- Storage
- Extraction

PELLETISATION

Wheat straw bale

ρ×30

pellets

$ScCO_2$ extraction

Wax products

Advantages:

- Further increase in density (×3)
- Decrease cost of transport/storage
- Increase quantity of material which can be fed in the extractor
- The extraction process (use of high pressures) will turn the pellets into powder

Straw powder

ECONOMICS

Assumptions:

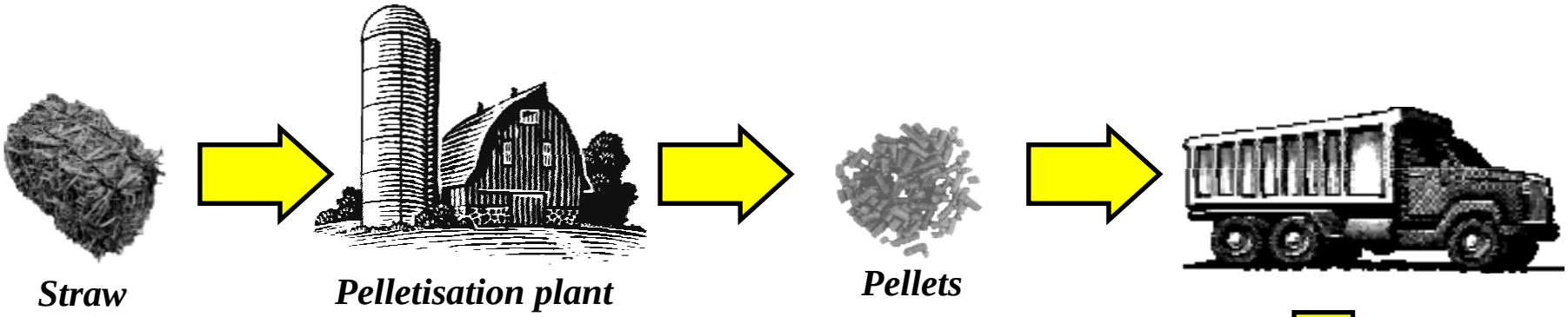
❶ Dewaxed material sold to power plant (existing market)

❷ No additional profit made from adding value to lignocellulose

Scenario	**1**	**2**	**3**
Extractor scale	Small	Large	Large
Pelletisation and extraction plant on same site	✘	✘	✓
Average wax yield (%)	1	2.5	2.5
Profits made from selling dewaxed straw	✘	✘	✘
Cost of extraction (€ / kg wax)	**220**	**62**	**35**

📖 *F.E.I. Deswarte, J.H. Clark, A.J. Wilson, J.J.E. Hardy, R. Marriott, S.P. Chahal, C. Jackson, G.. Heslop, M. Birkett, T.J. Bruce, G. Whiteley, Biofuels, Bioprod. Bioref.,1 (2007) 245.*

BIOREFINERY LOCATION



Straw

Pelletisation plant

Pellets

Plan A - biorefinery on the site of the pelletisation plant

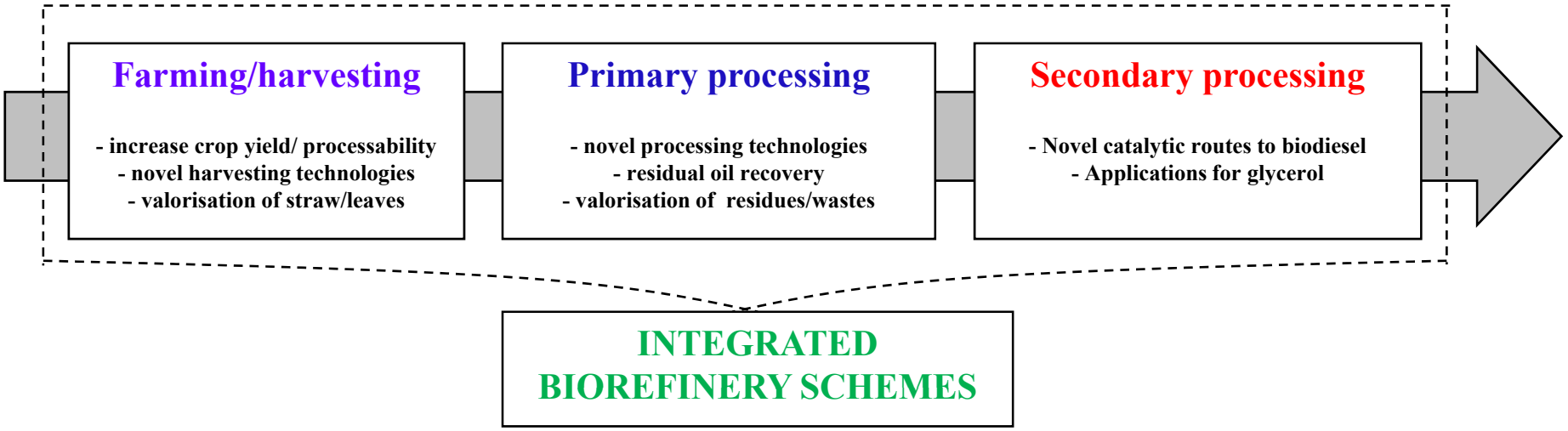
Power plant

Plan B - biorefinery on the site of the power plant

SUSTOIL

Developing advanced Biorefinery schemes for integration into existing oil production/transesterification plants

Scientific Coordinator - Dr Fabien Deswarte (feid100@york.ac.uk)



- Funded by the European Commission through Framework 7
- Coordinated by the Green Chemistry Centre, University of York
- Integrate the expertise of 22 project partners across 10 EU countries
- 2 year project starting on 1st May 2008

THANKS TO:

AND THANKS FOR YOUR ATTENTION!

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