ICS UNIDO

Energy & added value products from biomass

(opportunities & risks)

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Italy

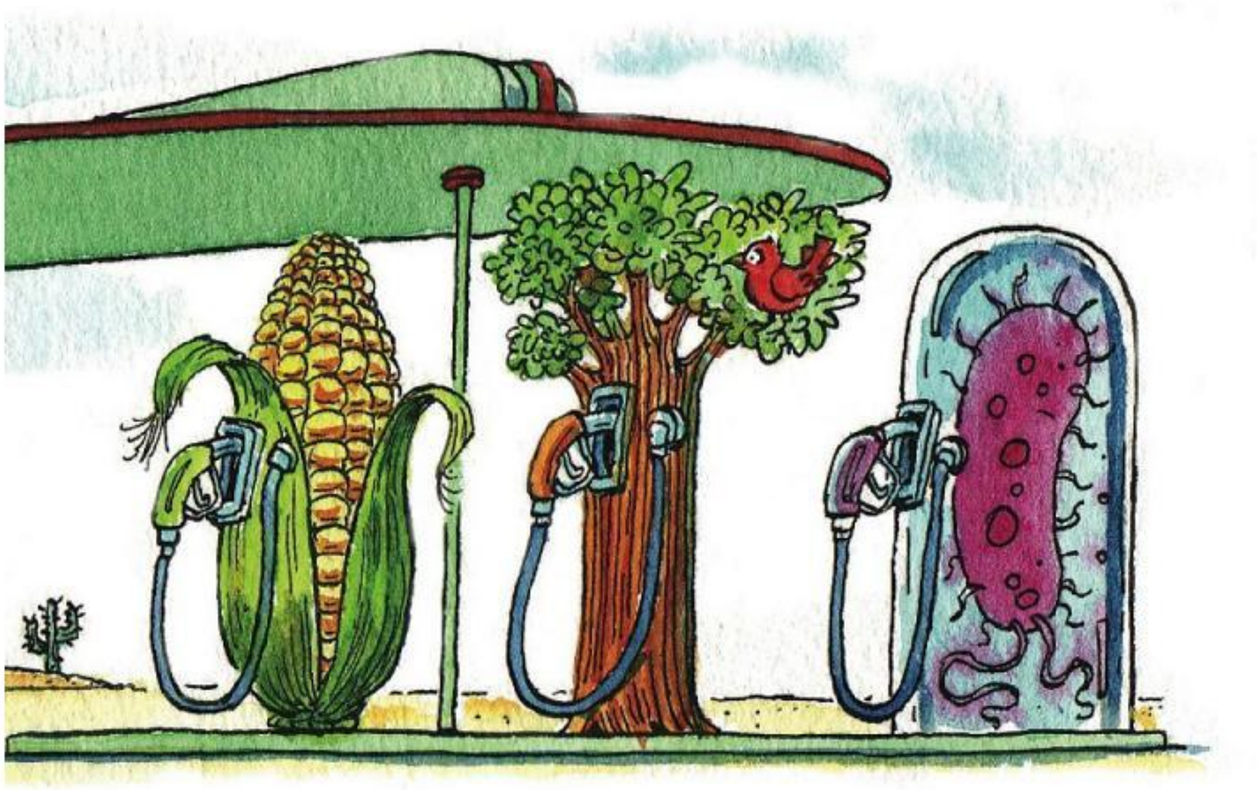
Presentation outline

- Introduction to next generation biofuels
- Some sustainability aspects (opportunities & risks)
- Brief on ICS UNIDO program and activities
- Selected research programs (including ICS-UNIDO)

Why biofuels and bio-based chemicals?

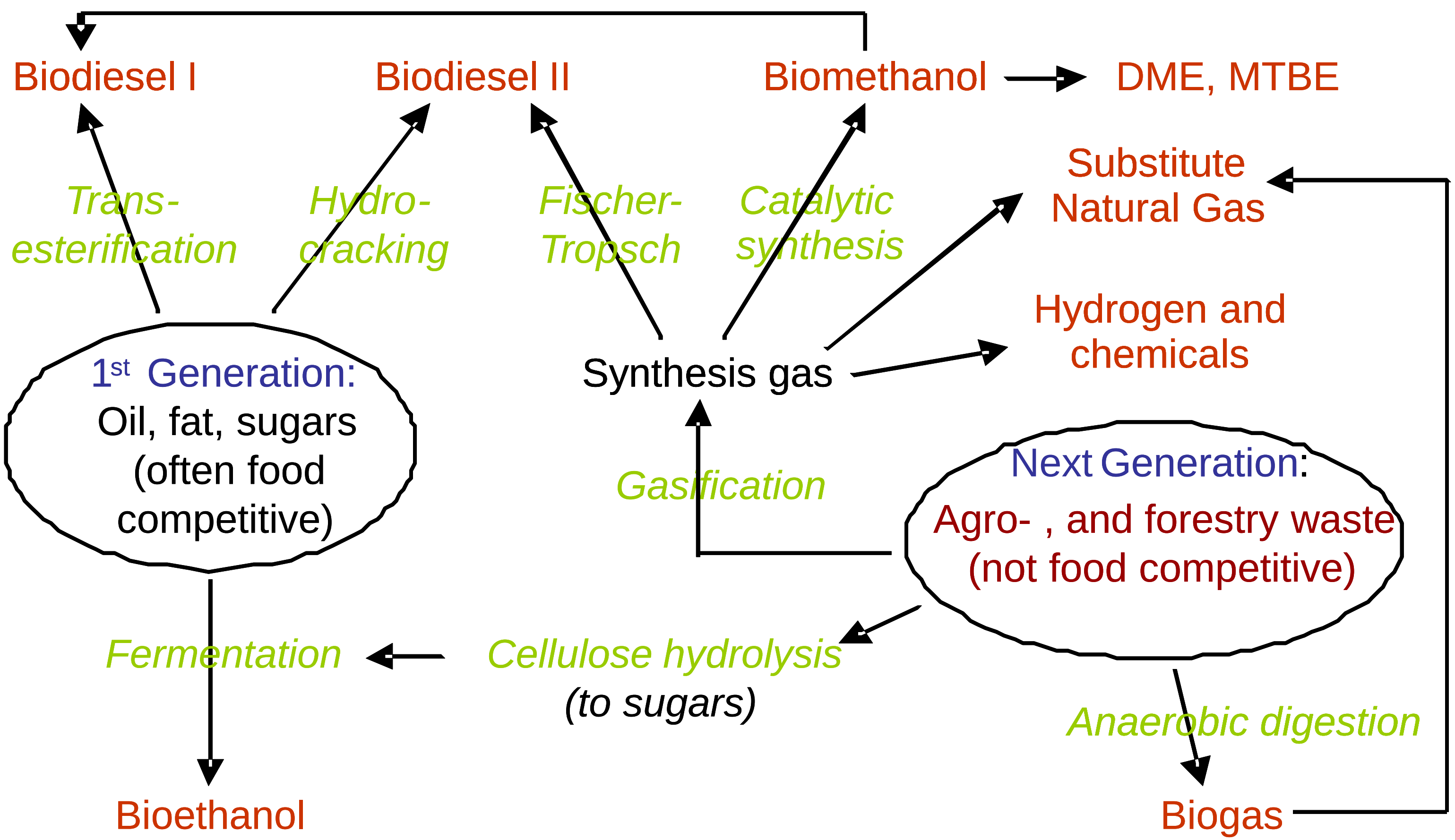
- Fossil fuel depletion
- Diversification of feedstocks (energy security)
- Kyoto Protocol (bio-feedstocks can be CO_2 neutral)
  /transition to low carbon economy/ Cop1nhagen, EU 20-20
- Stimulation of new green chemical industry development
- Valorization of waste biomass
- Integrated development of agriculture and industry
- Improvement of social economic conditions,
  especially in Developing Countries

Biofuels Generations

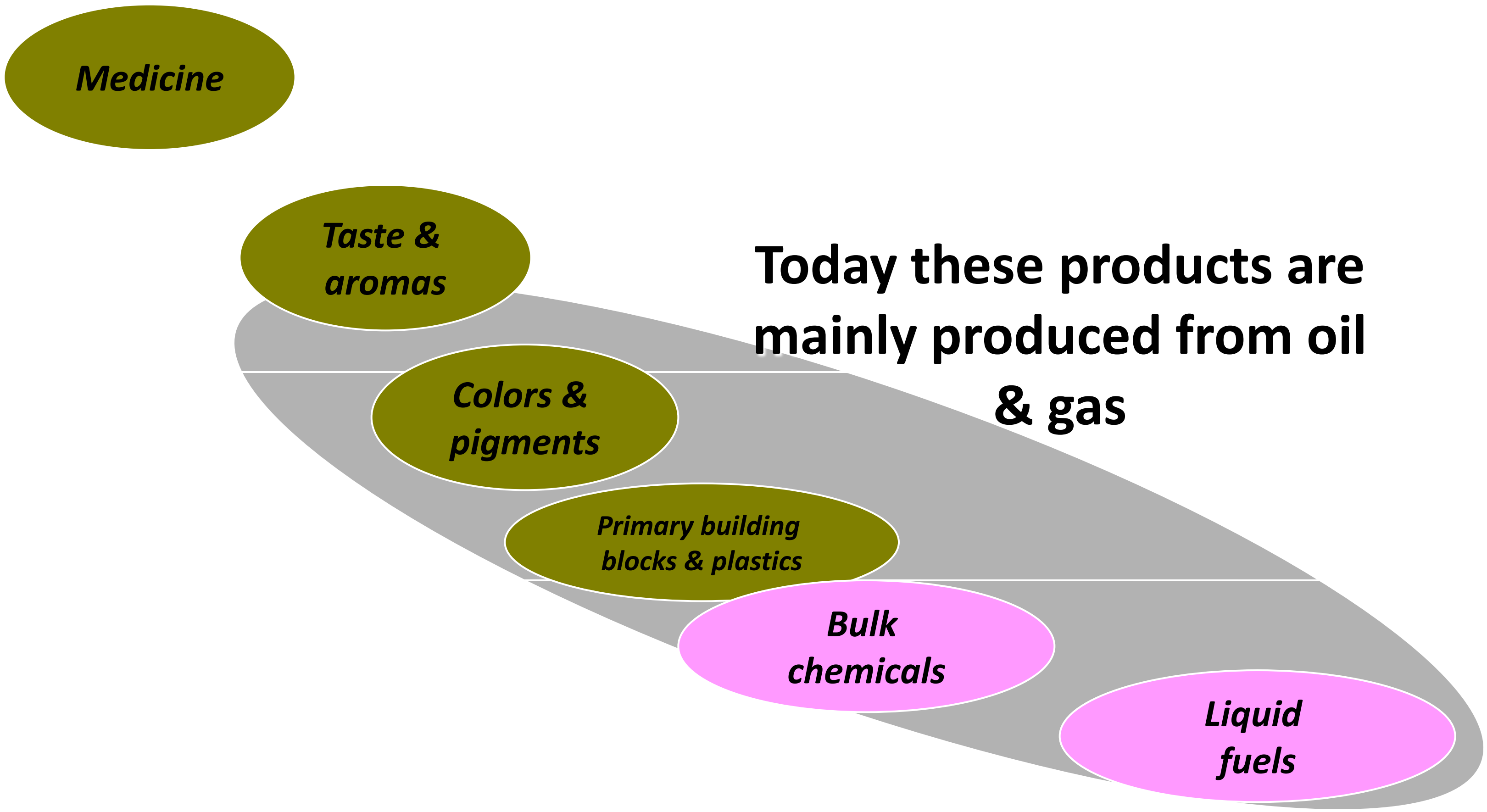


Nature (2008), p. 891

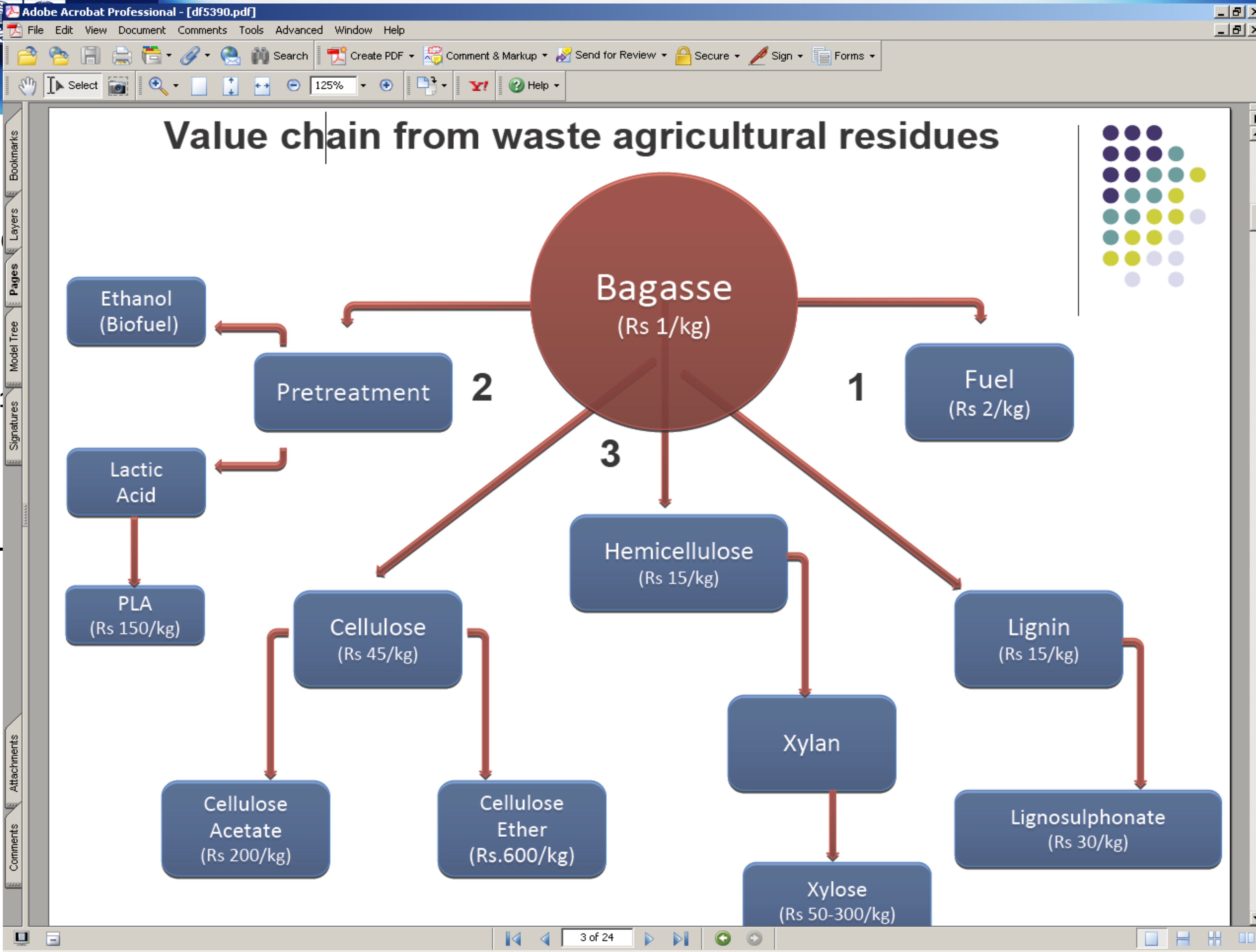
How? Processes and feedstocks



What? High Value Chemicals



Today these products are mainly produced from oil & gas



Price per ton

How? From agricultural waste:
Abundant feedstock for future processes

Agricultural by-products:
a Key Biofuel Source

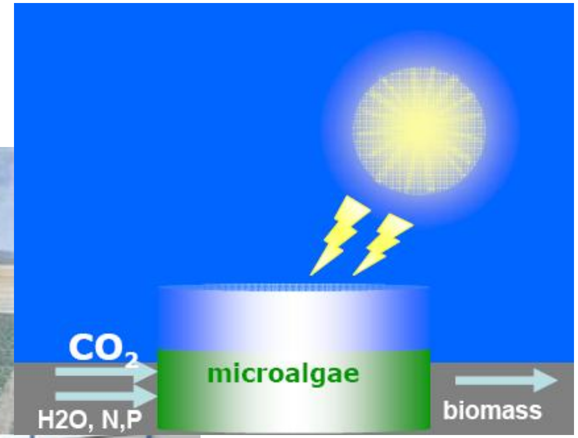
REGION	WASTE CROP	LIGNOCELLULOSE BIOMASS	TOTAL
EUROPE	5.45	63	69
N. AMERICA	0.87	63	64
ASIA	30	⇨ 261	291
AFRICA	5.3	10.8	16
S. AMERICA	5	30	35
TOTAL			491 GL

REPLACES 353 GL GASOLINE,

OR 32% WORLD-WIDE CONSUMPTION AS E85

Pyrolysis of oil palm residues in Malaysia

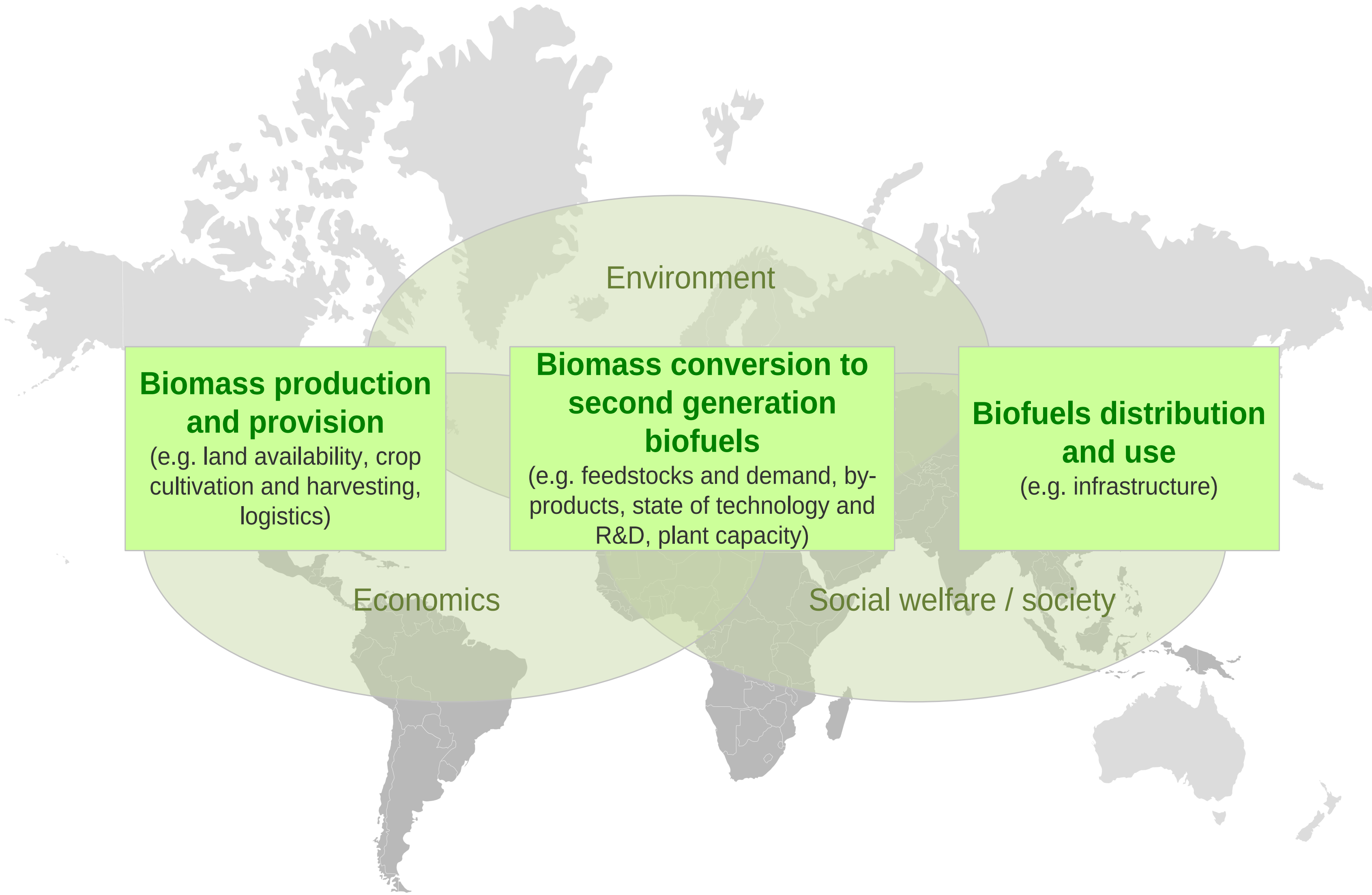
How? Algae biomass:
future feedstock for known processes



- About 2 Tons of CO2 are fixed per ton of biomass
- Cells can store sugars or lipids
- Microalgae can remove P, N compounds from water
- Tens times higher oil yield per Ha than oil crops

Background

Biofuel sustainability



Next generation biofu

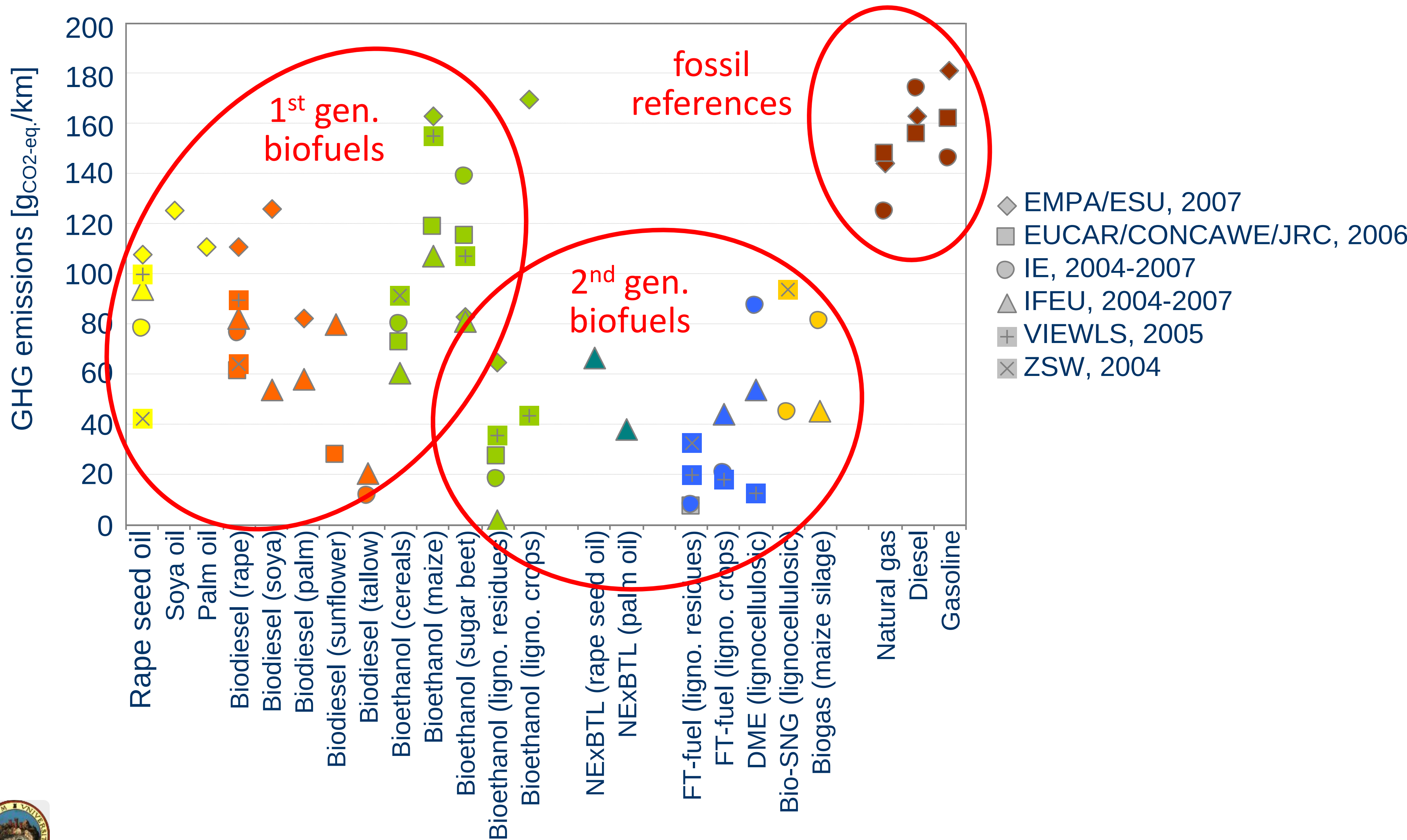
Overview

	HVO	Bioethanol	BTL (FT fuels)	DME	Biomethane / Bio-SNG	Biomethane / Biogas
State of technology[A] current in 2020	→→→(→) →→→→	→→→ →→→→	→→ →→→	→→ →→→	→→ →→→(→)	→→→(→) →→→→
Technical effort[B] (system complexity)	+++	++	+	++	+++	++++
Typical exp. plant capacity [$MW_{biofuel}$]	150 to > 800	15 to 185	> 130 to 500	> 130 to 340	20 to 170	5 to 15
Feedstock demand[C] for exp. plant capacity [1,000 t_{ar}/a]	300 (rape seeds) to 4,400 (palm, fresh bunches)	75 to 915 (straw) 60 to 735 (misc)	650 to 2,500 (wood / willow)	570 to 1,500 (wood / willow)	85 to 600 (wood /willow)	43 to 130 (maize sil.) 60 to 190 (biowaste)
Theoretical land demand for feedstock[D] [1,000 ha/a], examples	145 to 500 (rape seeds)	20 to 460 (straw)	25 to 280 (wood / willow)	20 to 170 (wood / willow)	3.0 to 70 (wood /willow)	0.3 to 1.0 (maize silage)
Exp. overall efficiency biofuel production[E] [%]	20 (soya) to 60 (palm)	45 to 50	40 to 45	55 to 60	60 to 65	45 to 85
Publicity Technology / concept provider[F]	public promoted as NExBTL by NesteOil (plant in FL, planned for SGP), promotion also by companies like BP	very public, esp. in US, EU, LA promoted by companies like IOGEN, ABENGOA, POET, COSAN	very public, esp. in D well promoted as Sunfuel by CHOREN, SHELL, VW, DAIMLER, TOTAL (pilot /demo plant, planned large-scale plant in D)	public, esp. in S pushed by CHEMREC based on black liquor in pilot plant in S, promotion also by VOLVO	increasing publicity (pilot plant in A, planned plants in S, D, NL) primarily SME, increasing interest for companies like E.ON	increasing publicity (many plants, e.g. in S, D, CH, NL) primarily SME, increasing interest for companies like E.ON

A: concept / laboratory →, pilot →→, demonstrated →→→, commercial →→→→ // B: less promising +, very promising ++++ // C, D: rough values for typical feedstocks and plant capacities under EU conditions // E: – theoretical values according to current state of development // F – examples // ar – as received free plant gate // HVO: Hydrogenated vegetable oil // BtL: Biomass to Liquid // SNG: Synthetic Natural Gas

Environmental assessment

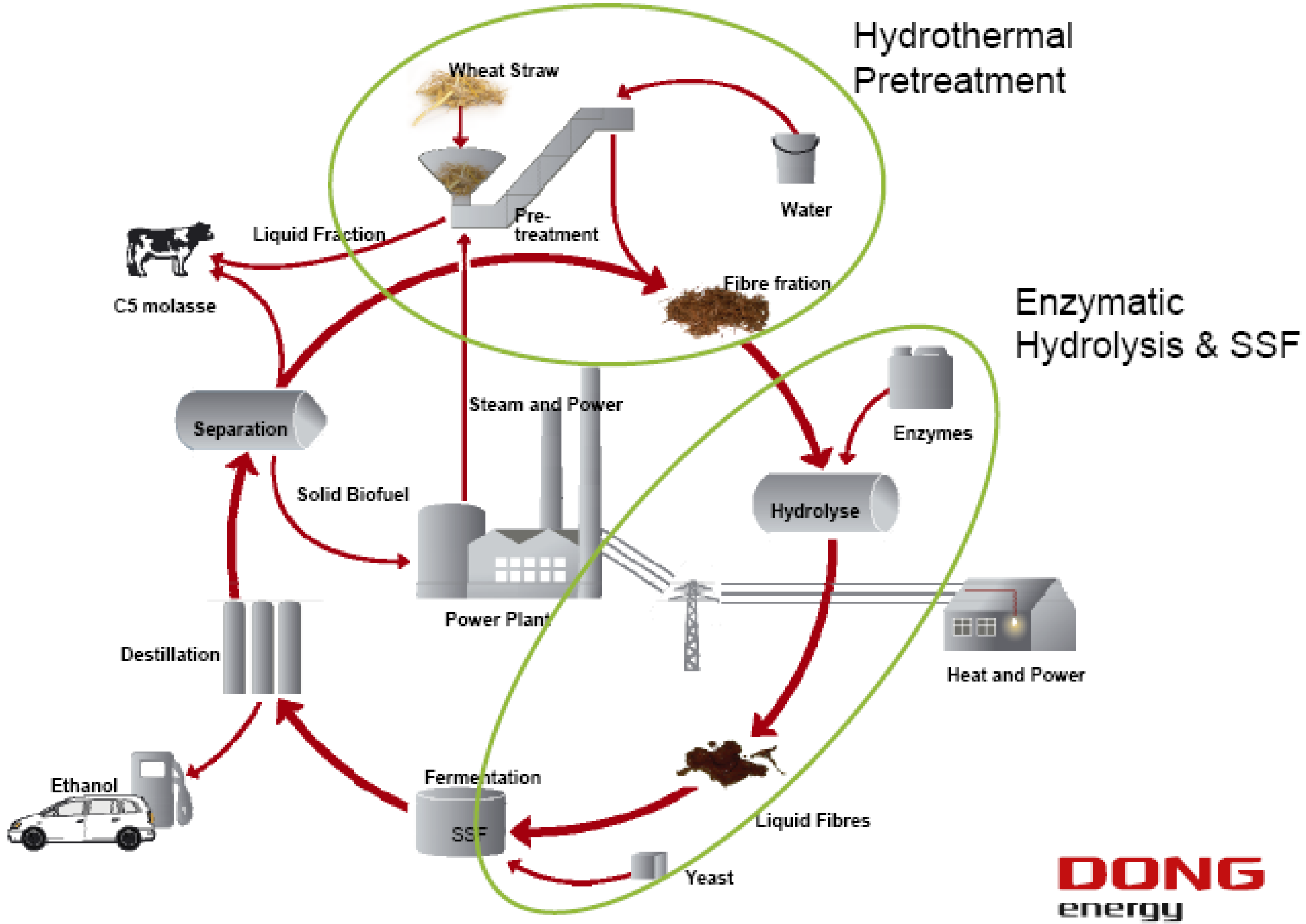
Global warming potential



Source: DBFZ / IE Leipzig, 2007, diverse Studies

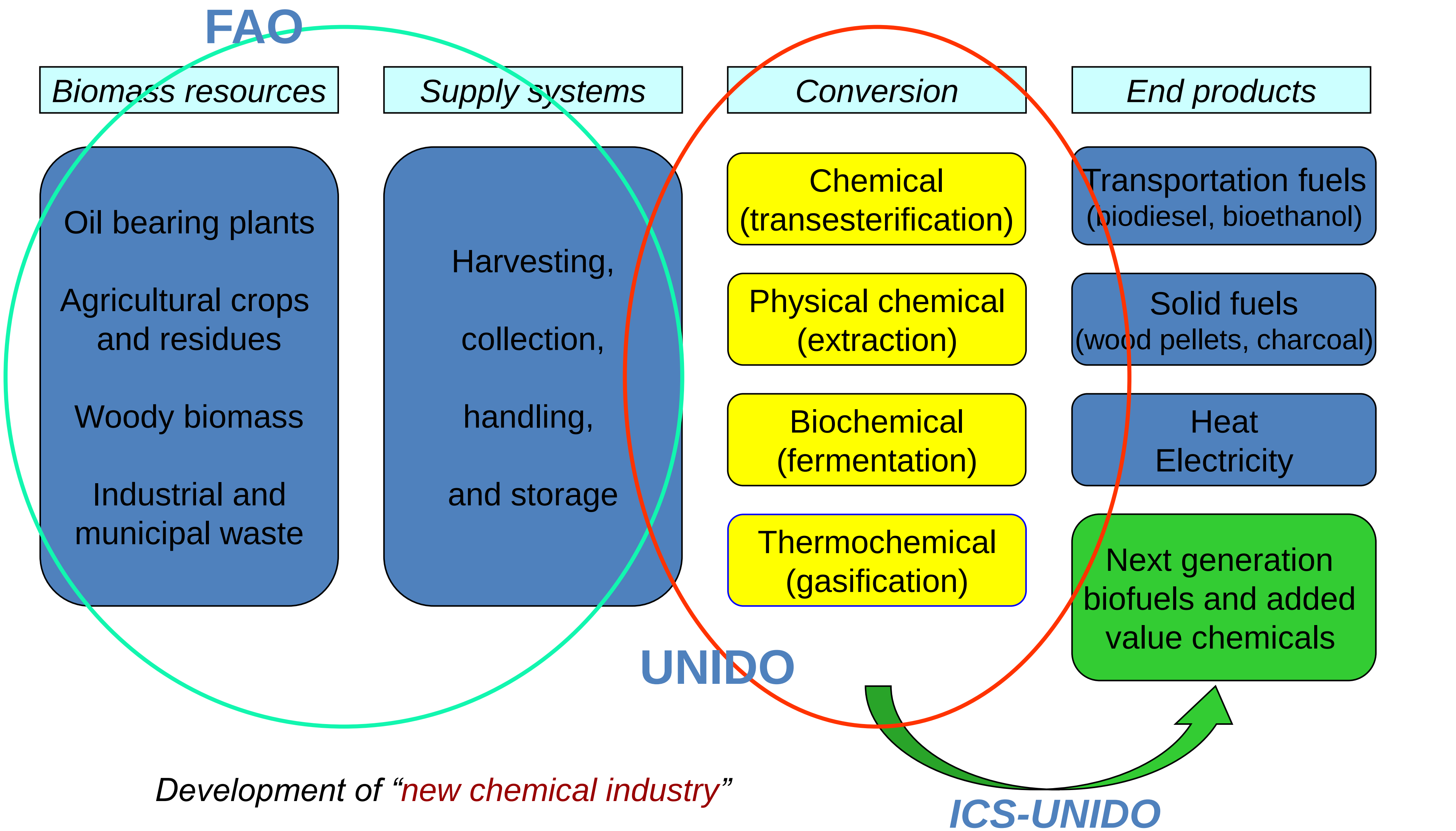
Inbicon Biomass Refinery

The IBUS Process



DONG energy

Biofuel value chain and UNIDO radius of attention



ICS UNIDO core programmes and projects

- NEXT GENERATION BIOFUELS AND BIOREFINERY
  - Next generation biofuels
  - Biorefinery (biobased products)

- GEOTHERMAL ENERGY
  - **Exploration and monitoring of resources**
  - **Energy recovery and power plant technology**

- RATIONAL DESIGN OF DRUGS AGAINST PANDEMICS
  - **Computer Design of Potential Drugs against Malaria, TB and Dengue**
  - **Synthesis and activity assays of potential drugs against Malaria, TB and Dengue, designed by computer modelling**

- NANO-DRUG-DELIVERY AND NANO-DIAGNOSTICS
  - **Development of Targeted Nano-Particle-Based Drugs for orphan diseases using polymer coatings and particle-cell interactions measured using optical tweezers**
  - **Development of innovative low cost diagnostic methods using state-of-the-art nano-fluidics and nano-pore technology combined to give nano-arrays for high sensitivity proteomics**

ICS-UNIDO focus: Feedstocks for next generation biofuels & bio-based chemicals

- Non-food & waste
  - Lignocellulose from wood and woody waste (saw dust, wood chips)
  - Agro-waste (bagasse, rice husk, coffee waste, ...)
  - Oils from algae
  - Oily waste (waste cooking oil, fats, spent coffee)
  - By-products of bio-based production (glycerol, press cake, FFA, lignin residues, black liquor, ...)

ICS-UNIDO activity tools with target on the outcomes in developing countries

ICS-UNIDO
(international Centre for Science and High Technology),Trieste, Italy
(funds by Italian Gov. to UNIDO)

Research activities

- **promotion and implementation of research projects**

Fellowship program
(6 -12 months on job training), participation in research projects

Capacity building

- **training courses, workshops**
- **e-learning programme (DVDs from TC, WSPs,..)**

ICS-UNIDO Global Network **on biofuels and bio-based chemicals**
(centres of excellence in developing countries and in industrialized countries)

see also **http://www.ics.trieste.it/core-programmes/biofuels.aspx**

Events 2006-2009:
Technologies for Renewables Exploitation

- EGM on Technologies for Exploitation of Renewable Feedstock and Waste Valorisation, 20-30 May 2006 Trieste, Italy
- Workshop on Bio-fuels: emerging technologies and their assessment 4 July 2007, Sustainable Plastics and chemical products from renewable resources Malaysia
- Workshop on Biofuels: R&D Technologies for a sustainable development in Africa Accra, Ghana, December 2007
- Special Session on Biofuels and Chemicals from Bio-resources (within the UNIDO Conference on Renewable Energies) 14-18 April Dakar, Senegal
- Workshop on Biofuels and bio-based Chemicals Trieste, Italy 18-20 September 2008
- Workshop on Sustainable Plastics from renewable resources and from agro-food waste Cairo, Egypt March 2008
- Workshop on Biofuels, Chemicals and Polymers from bio-resources Santa Fe, Argentina 28-30 October 2008
- Workshop on Next Generation Biofuels and bio-based Chemicals Trieste, Italy 21-23 April 2009
- Seminar Next Generation Biofuels and bio-based Chemicals Trieste, Italy 24 April 2009
- Training Course on Chemistry and Technology for biofuels, bio-based products, and chemicals from biomass Italy, 21-26 September 2009

- DVDs

ICS-UNIDO selected review publications 2008-2009

Survey of Future Biofuels and Bio-based Chemicals, ICS UNIDO Publication 2008, available at www.ics.trieste.it

BIO-FUELS: Technology Status and Future Trends, Technology Assessment and Decision Support Tools, ICS UNIDO Publication 2008, available at www.ics.trieste.it

A chance to biofuels for a chance to Africa. Will the technology make change? S. Zinoviev and S. Miertus, Chimica & Industria 05 2008, 106-112

EMERGING TECHNOLOGIES FOR THE NEXT GENERATION BIOFUELS: Survey and assessment of technical, economic and environmental aspects
F. Mueller-Langer, S. Zinoviev, G. Centi, P. Fornasiero, M. Kaltschmitt, S. Miertus ChemSusChem 2010,.

Catalytic Applications in Biodiesel Production from Vegetable Oils: A Review
A. Sivasamy, F. Kemausuor, P. Fornasiero, K.Y. Cheah, S. Zinoviev, S.Miertus ChemSusChem 2009, 2, 278-300.

Some examples of ICS-UNIDO join research projects

1. ***Photo-catalytic reforming and aqueous phase reforming of glycerol***

2. ***Catalytic upgrading of furfural and derivatives***

3. ***Lipase catalyzed transesterification of waste oils***

4. ***Lignin degradation with laccases***

5. ***Molecular modeling of enzymatic lignocellulose hydrolysis***

Catalytic technologies for production of biohydrogen from glycerol and sugars by thermal reforming

(in collaboration with University of Trieste, INCAPE-Argentina, and Loyola College of Chennai-India)

Novelty and motivations

- *General scope*
  - Contribute to the development of novel catalytic processes for H_2 production from biomass-derived feedstocks
- Motivations
  - H_2 is important for the industrial chemistry and as potential energy vector. The production of H_2 from renewable sources has some advantages such as:
    - Reduction of the dependence from fossil fuels, increasing energy sustainability and reducing CO_2 emissions (lowering greenhouse gas emissions).
    - Valorization of by-products (glycerol) and agro-food residues to produce added value products (with increment in the economy of the territory)
    - Develop routes to energy starting from non-edible materials.

Catalytic technologies for production of chemicals from lignocellulose

(in collaboration with University of Messina, Women's Christian College of Madras-India)

Novelty and motivations

- *General scope*
  - Contribute to the development of novel chemo-catalytic approach to ligno-cellulosic biorefineries
- Motivations
  - Ligno-cellulosic waste biomass constitute a great opportunity, particularly for developing countries, to produce fuels from waste products, with the multiple objective of
    - Produce valuable energy products reducing the dependence from outside resources, increasing energy sustainability, and reducing CO_2 emissions (lowering greenhouse gas emissions)
    - Valorization of agro-food residues to produce added value products (with increment in the economy of the territory)
    - Reduce the impact on the environment of food production and disposal of large volumes of biomass residues
    - Develop food non-competitive routes to energy products

Strategy for novel chemo-catalytic biorefineries

Lignocellulose raw material

Acid catalysis hydrolysis
- Novel processes using solid catalysts

Novel platform molecules

Furfurals (furfural from pentoses and HMF – 5hydroxymethyl furfural from hexoses)

Furan resins, monomers for high performance polymers (2,5- dicarboxy furan), etc.

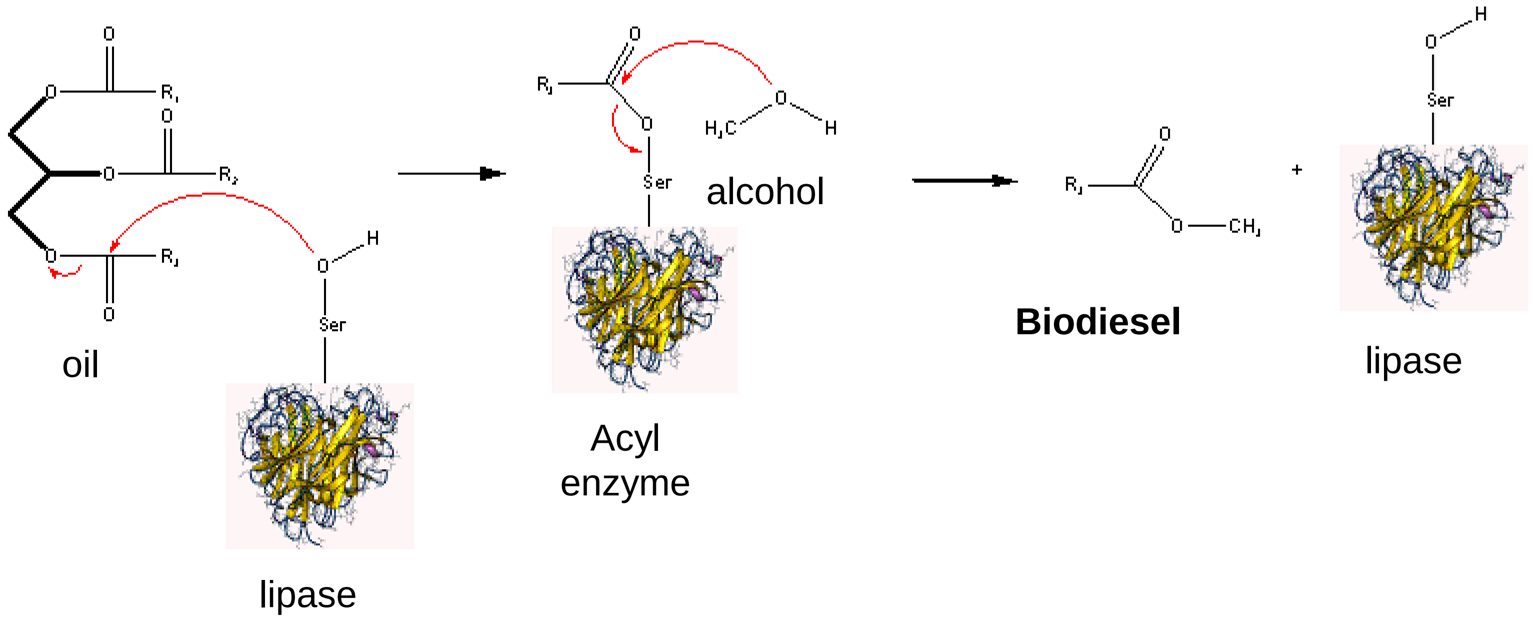
Biofuels:
- gasoline [octane boosters, e.g. methyl furans]
- biodiesel (by reaction with bioethanol)

Chemicals
- Levulinic acid and its products, select. oxidative esterific. for fine chyemicals – alkyl furoate, etc.)

Immobilized Lipases for catalytic transesterification of waste oil

(in collaboration with University of Trieste, SPRIN Trieste, and University of Malaya)

Enzymatic synthesis of biodesel: advantages



a) possibility of using waste oils and oils containing fatty acids
b) use of steichiometric amounts of the alcohols
c) reduction of wastes
d) mild and neutral reaction conditions
e) higher purity of the glycerol obtained as secondary product

Objectives

What is needed for enzymatic synthesys of biodiesel

- Robust lipases resistant to methanol denaturation
- High activity
- Efficient immobilization methods
    - enzyme stabilization
    - good immobilization yield
    - prevention of biocatalyst aggregation
    - prevention of methanol/glycerol adsorption

Strategy

- selection of immobilization support
- developing an immobilization protocol with the aid of statistical methods
- application to biodiesel production

Degradation and valorization of lignin by laccases:
Activity and stability of laccases under different experimental conditions

(in collaboration with University of Trieste and Russian Academy of Sciences, Moscow)

Lignin

Lignin, a highly branched, irregular three-dimensional organic polymer is the most abundant biopolymer in Nature next to cellulose and the only one based on aromatic monomers. The complex nature of lignin makes difficult processing and modification. Lignin is degraded by fungi of diverse taxonomic groups, of which the white rot basidiomycetes are the most efficient in this respect. These white rot fungi produce several types of redox enzymes, including laccase. Laccase (benzenediol: oxygen oxidoreductase, EC 1.10.3.2) belongs to a group of polyphenol oxidases containing copper atoms in the catalytic centre and usually called multicopper oxidases. Laccases typically contain three types of copper, one of which gives it its characteristic blue colour.

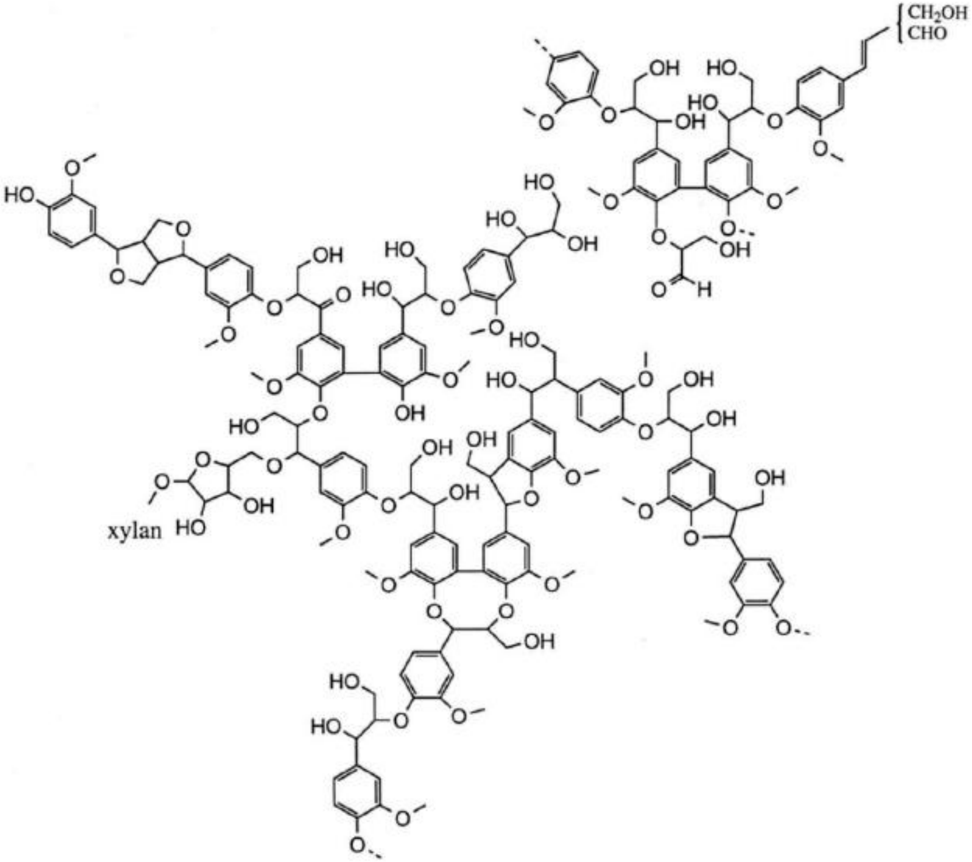
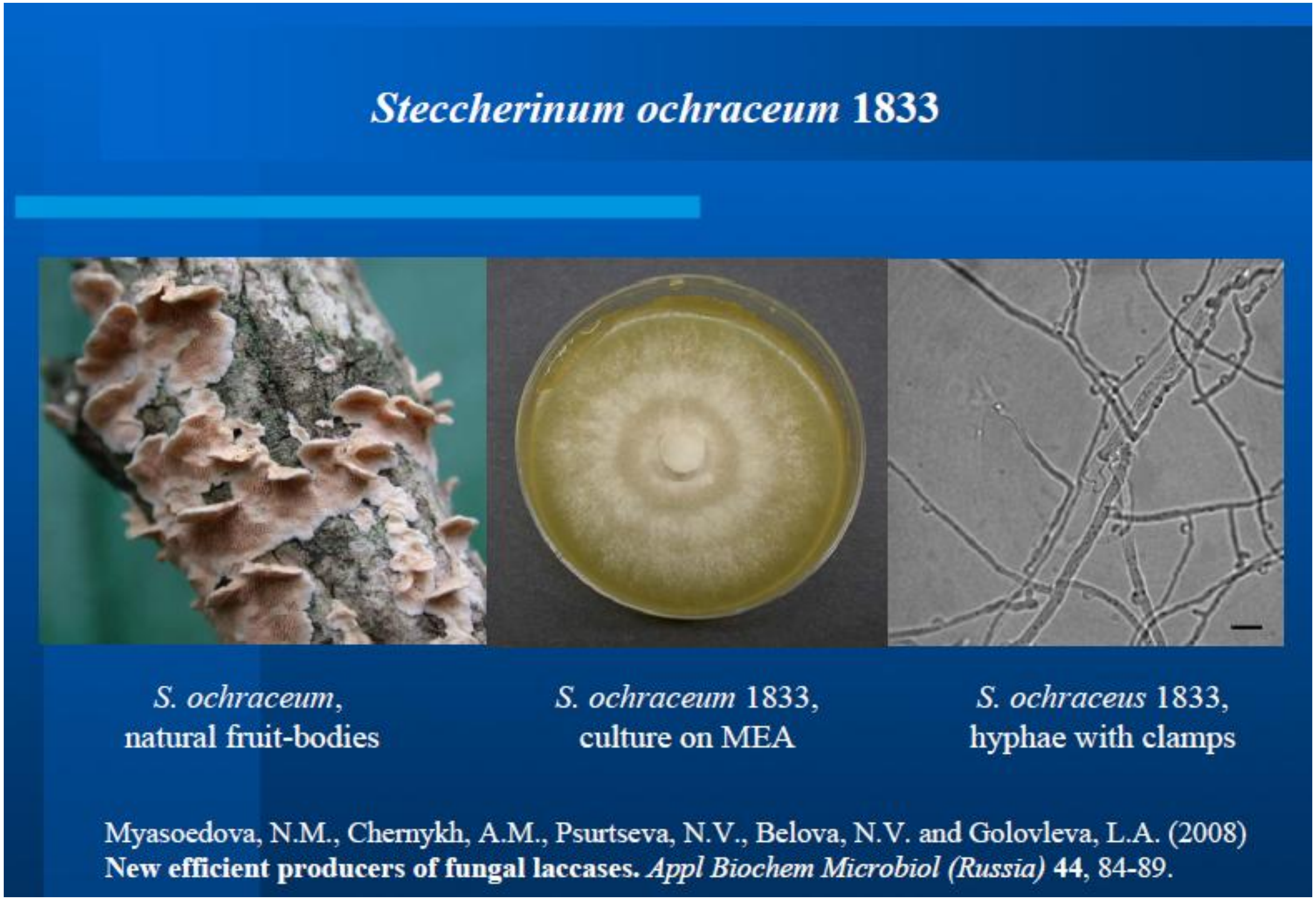


Fig. 4. A structural model of softwood lignin according to Brunow *et al*., 1998.

Motivation and novelty



- **Laccases** catalyze the reduction of oxygen to water accompanied by the oxidation of a substrate, such as methoxy-substituted monophenols, *o*, *p*-diphenols, aminophenols, polyphenols, polyamines, aryl amines and lignin

Objectives

Aim of the work:

Identify laccases able to preserve their activity under conditions which can favour the accessibility of the enzyme to substrates (e.g. organic solvents, microwaves)

Experimental Tasks:

•Evaluation of activity and stability of the studied laccases in the presence of organic solvents.

•Investigation of the stability of laccases under the action of microwave irradiation.

•Characterization of different types of lignin samples through determination of phenolic hydroxyl content.

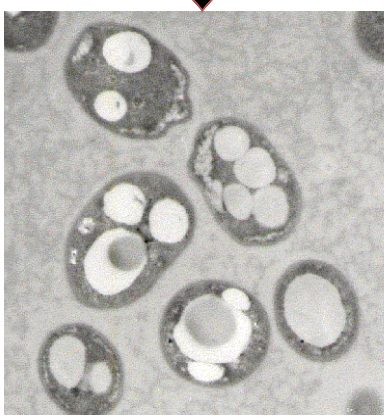
•Evaluation of changes in lignin structure after the treatment with laccases.

Projects for green plastics

(China, Indonesia, Austria, Brazil, Thailand, East Europe)

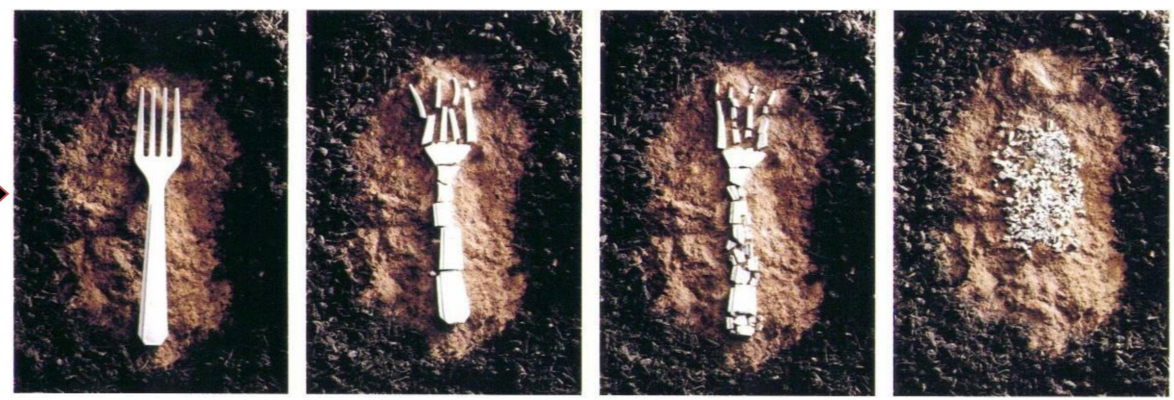
2008 – GREENOLYMP
Green Olympic Games, Beijing,
Project proposal in collaboration with Chinese Institutions
(Tsinghua University, Chinese Olympic Committee)

Agro-food waste



Alcaligenes latus

Cells for the production of environmentally degradable plastics



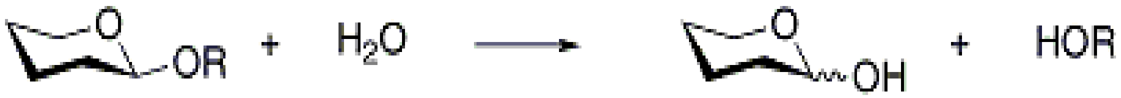
1st to 45th day

Computational Studies on Glucosidases for Cellulose Hydrolysis

(in collaboration with IUCT of Mumbai-India)

Glycosyl hydrolases

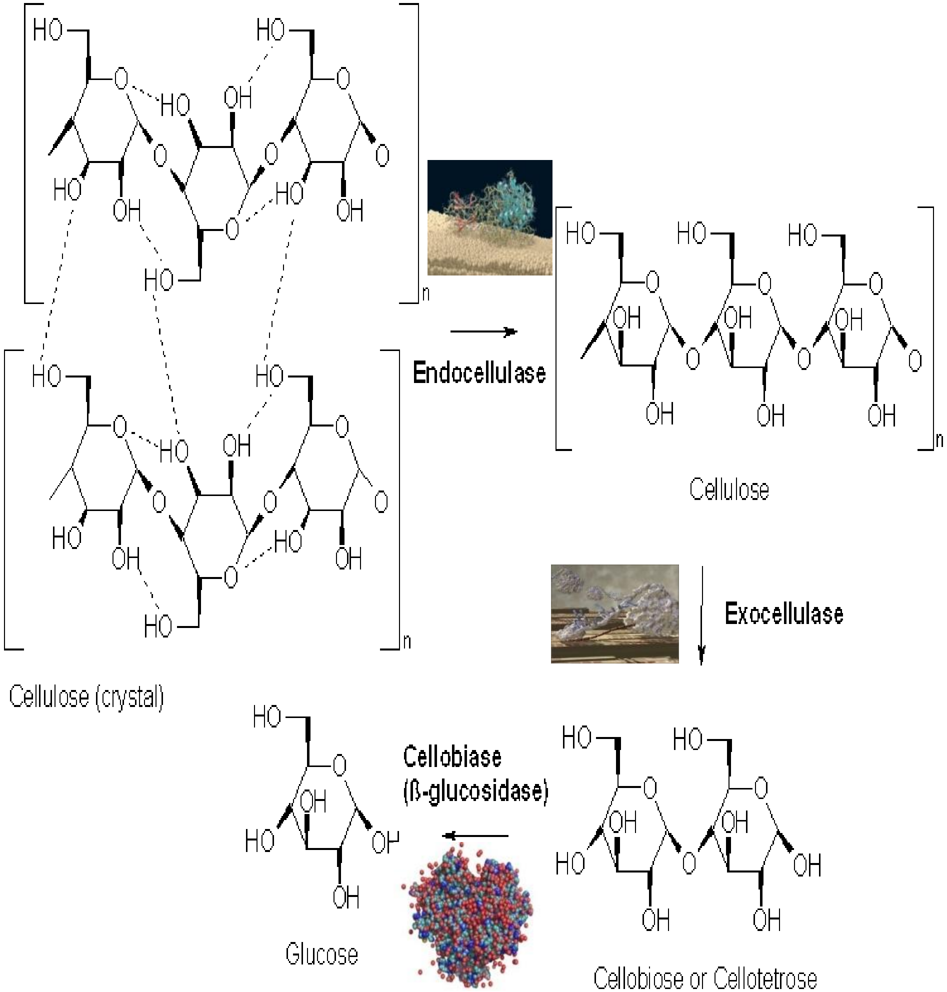
- Enzymes responsible for hydrolysis of glycosidic linkage



- These are ubiquitous enzymes and are involved in varied functions
- Together with glycosyltransferases, glycosiylhydrolases form the major catalytic machinery for synthesis and breakage of glycosidic bonds
- Ethanol for 2nd generation biomass involves hydrolysis by glycosylhydrolases to glucose and xylose for fermentation requirements
- Current costs of producing required hydrolytic enzymes are at USD 0.25–0.45 per gallon of ethanol making it uneconomical

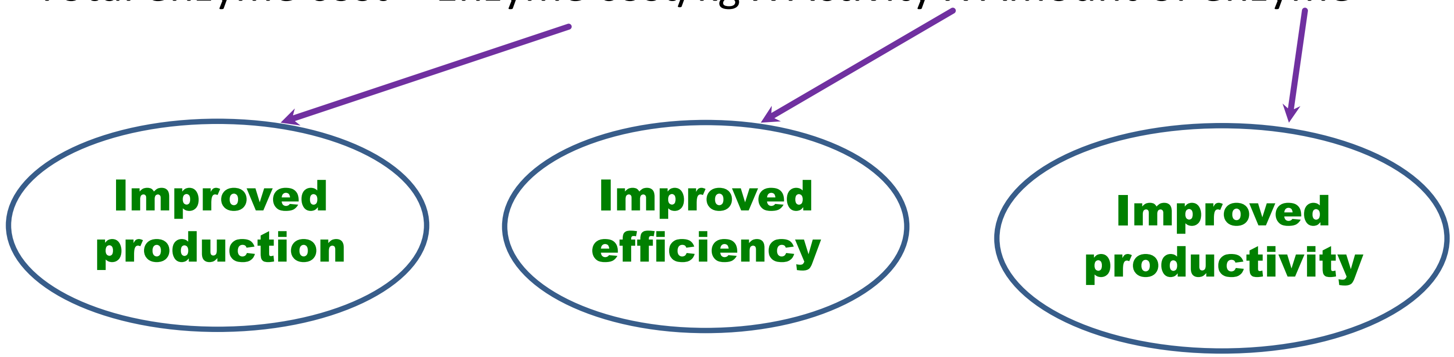
Enzymatic hydrolysis of cellulose

- Found in aerobic cellulose-degrading bacteria and fungi
- Consist of a synergistic set of three soluble enzymes having varied substrate specificities:
  1) Endoglucanases, which randomly hydrolyze β-1, 4-glycosidic linkages at the interior of a cellulose fiber
  2) Cellobiohydrolases, which cleave cellobiose units from the ends of a cellulose fiber;
  3) β-glucosidase, which hydrolyzes cellobiose into its constituent glucose monomers



Saccharification Enzymes

Total enzyme cost = Enzyme cost/kg X Activity X Amount of enzyme



Issues associated

Structural features of the substrate and enzyme – Non-productive binding

End-product inhibitions

Kinetic rates of reactions for independent enzymes

Requirements

Enzymes working in synergy with high overall reaction rates, increased thermostability and reduced recalcitrance

Work needed

Rational Enzyme Engineering

Concoctions of glycosyl hydrolases - Increased Efficiency and Productivity

Objectives

Long term :

Redesign cellulases to be used efficiently in technologies aimed to harness sugars from lignocellulosic materials

Short term :

Develop structural explanations for non-productive binding and **end product inhibitions that reduce catalytic efficiency of known cellulases**

Define minimum essential structural modules that effect catalytic functions in cellulases

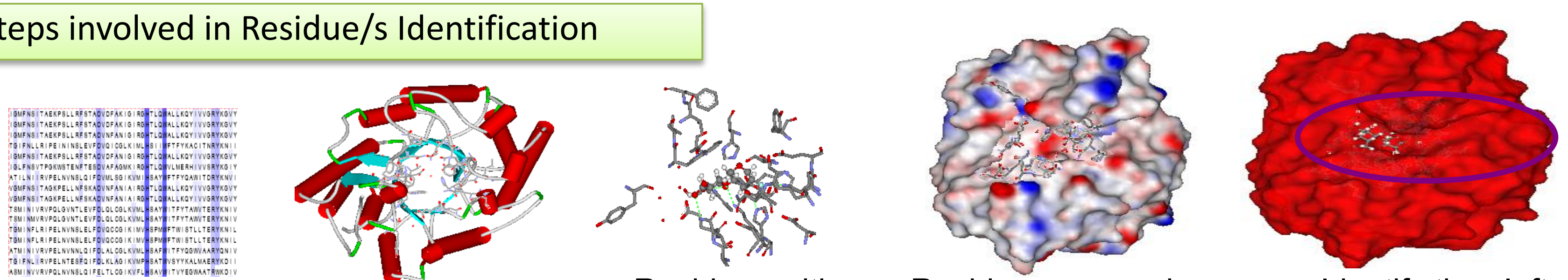
Design synthetic cellulases with multiple binding and catalytic domains *in silico*

Develop a range of multi-module "designer cellulases" capable of breaking the polysaccharide to reducing sugars

Model selection and analysis

- Among glucosidases belonging to $(\beta/\alpha)_8$ fold, enzymes of *P. chrysosporium* are highly efficient for hydrolysis of cellobiose and cellobiolactone
- BGL1A (β–glucosidase) shows relatively high sequence identity (50–60%) to biochemically characterized GH1 BGLs
- With a small tunnel-like active site pocket, formed by loops of the barrel, the catalytic residues of BGL1A are Glu365 (nucleophile) and Glu170 (acid–base)
- With distorted substrates, an extensive network of direct hydrogen bond(s) with the side chains of Gln20, His123, Asn169 and Glu422

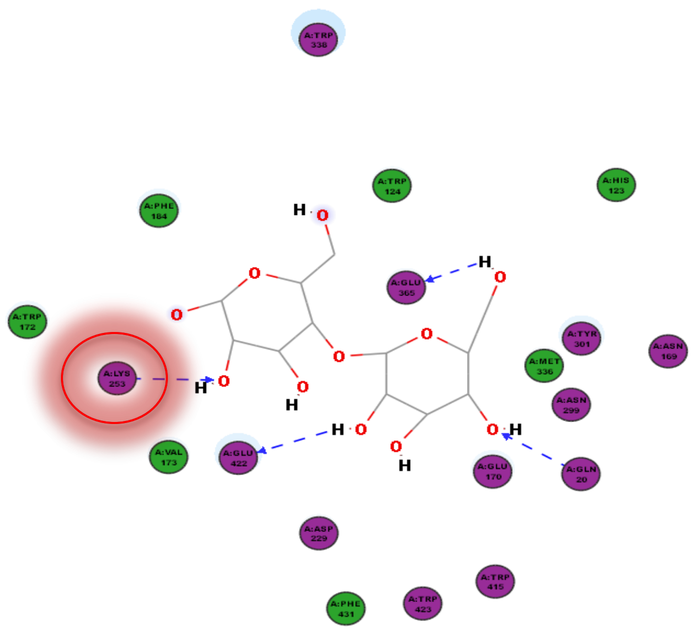
Steps involved in Residue/s Identification

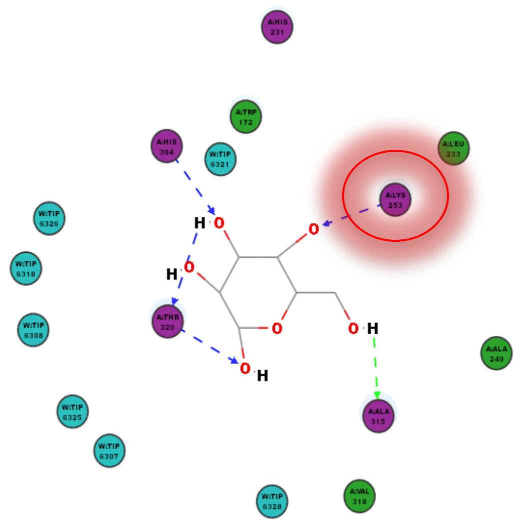


Sequences | Structures | Residues with >80% identity | Residues mapped on protein surface | Identify the cleft beyond the active site

Docking studies for glucose and cellobiose

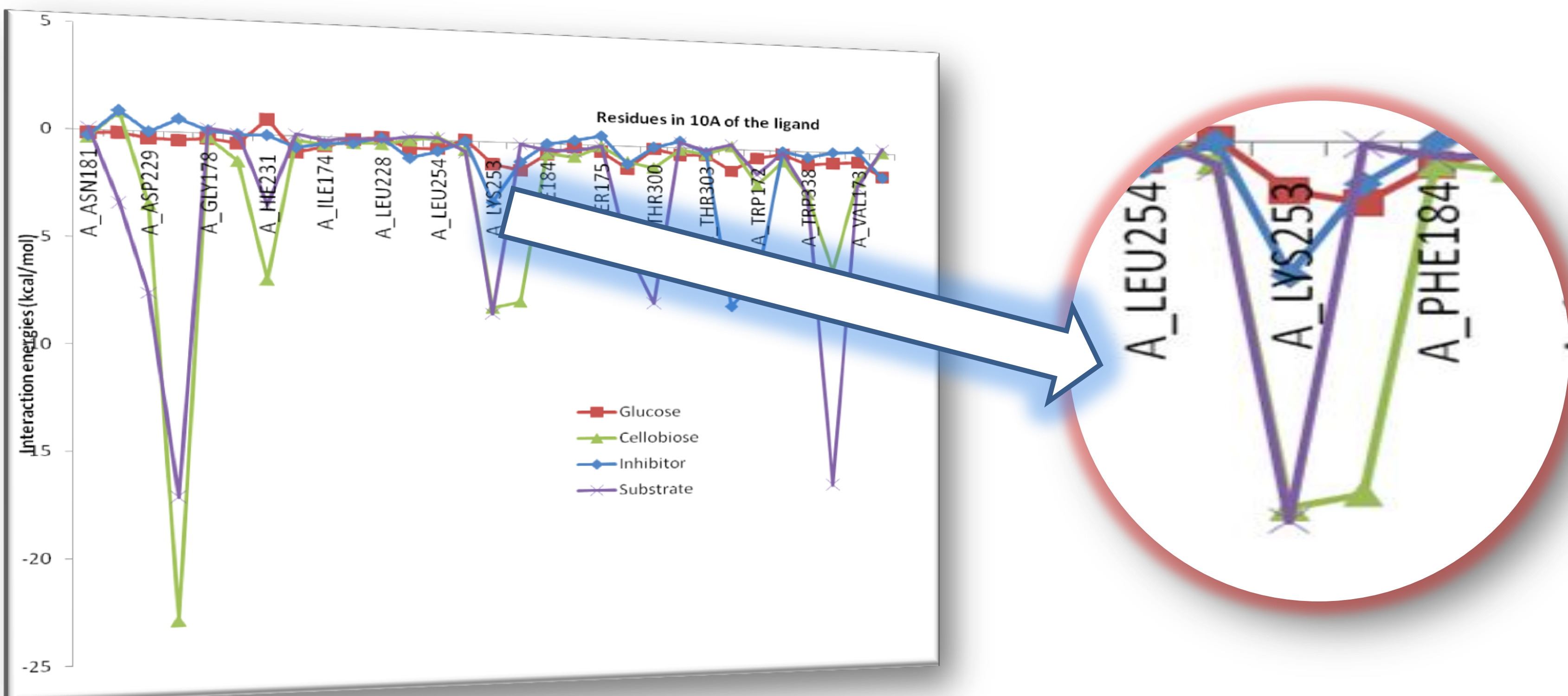
- BLG1A was selected as the model
- Substrate - cellobiose and inhibitor - glucose were docked for their poses and potential interacting residues at the active site
- Lys253 was observed to contribute highly to the interactions between cellobiose, the substrate and the protein and also glucose, the inhibitor and the protein
- The residue maybe important in the activity of the enzyme and its blocking by interactions with the inhibitor





Simulations for glucose and cellobiose at respective pockets

- MD simulations of 1ns were carried out four systems, namely, the apo enzyme, the substrate bound enzyme, the inhibitor bound enzyme and the enzyme complex with both the substrate and the inhibitor
- With implicit solvent conditions, the systems were allowed to proceed for 300ps after which snapshots were collected at every 20ps interval
- The interaction energy for each of the contributing residue within 10Å was evaluated and averages for the residue contributions towards total interacting energy have been plotted



Large initiative “ICS-UNIDO – ACP– EC/S-S” (project under preparation)

Next Generation Biofuels and Biorefineries for ACP countries

(to submitted fo UEC /DG – Cooperation)

Research,

Capacity building

Pilot plants

Networking

3-4 years (2011-2014), approx. 40 mln. Eur

Topics

Biofuels

- Biogas technology
- Biohydrogen by reforming of bio-based chemicals
- Biodiesel by transesterification of oils from algae, jatropha, and waste oils
- Gasification and pyrolysis of biomass, including agro-waste and forestry waste and further syntheses based on bio-syngas
- Enzymatic hydrolysis of cellulose from agro-waste and forestry waste and further transformation of sugars to alcohol fuels

Biorefineries

- Bio-based plastics from agro-waste
- Enzymatic degradation of lignin (by-product of agro-waste and forestry waste treatment) and further transformation of related products to chemicals
- Catalytic hydrolysis of cellulose from agro-waste and forestry waste and further transformations of its products to chemicals
- Liquefaction of lignocellulose from agro-waste and forestry waste and valorization of related products to chemicals and polymers

Pilot plants set up

- Plant for agro-waste
- Plant for sisal waste
- Plant for woody waste
- Plants from algae/water hyacinte

African partners (target: 25 partners from 20 states)

Ghana – CSIR

- Ghana – KNUST
- Ethiopia – Addis Ababa
- Sudan - IRCC
- Tunisia - CBS
- Egypt – NRC
- Egypt – Tanta
- Egypt – Alexandria
- Benin – Songhai
- Madagascar – consortium
- Namibia – University
- Mauritius - University

- Tanzania – Tatedo
- Tanzania - TIRDO
- Tanzania – SUA VET
- Cameroon - ISSEA
- Malawi - CARD
- South Africa – NEPAD
- South Africa - UNAM
- Zambia – BA
- Zambia – CEEEZ
- Zambia - UNZA
- Uganda – UIRI
- NIGERIA – F.U.T.

EU/other partners (to be completed)

- DBFZ (German Biomass Research Center), Germany
- University of Trieste, Italy
- University of Messina, Italy
- University of Florence, Italy
- Institute of Chemistry, Slovenia
- Technical University of Graz, Austria
- Växjö University, Sweden
- Dong Energy, Denmark
- Novozymes, Denmark
- Slovak Technical University of Bratislava, Slovakia
- Shell Global Solutions International
- Institut de Recherches sur la Catalyse, France
- Instituto de Tecnología Química de Valencia, Spain
- China (Tsingua U.) , India (U. Mumbay, NCL)
- Brasil (Petrobras), Malaysia (MPOB)

THANK YOU

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