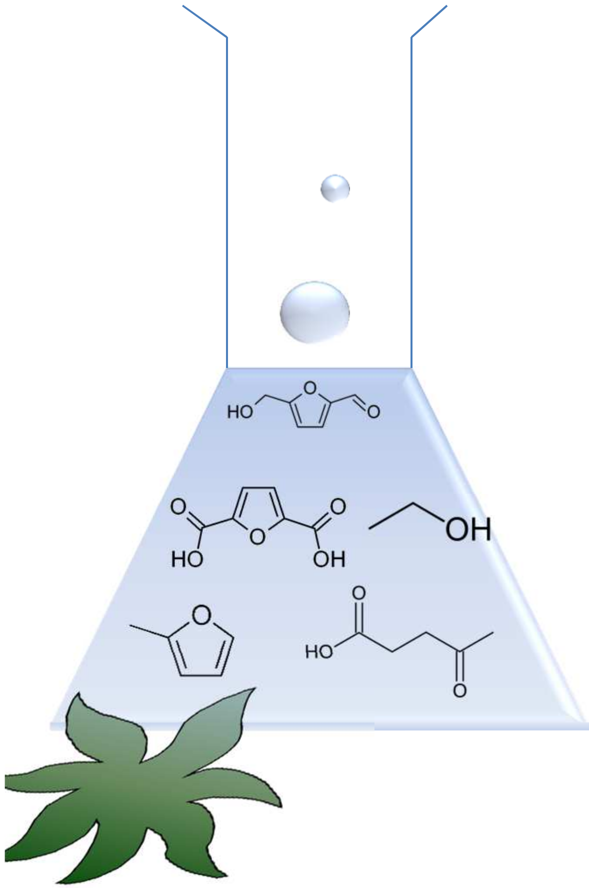
LIGNOCELLULOSICS-DERIVED CARBOHYDRATES AS PLATFORM MOLECULES FOR THE PRODUCTION OF BIOFUELS AND BIOBASED PRODUCTS



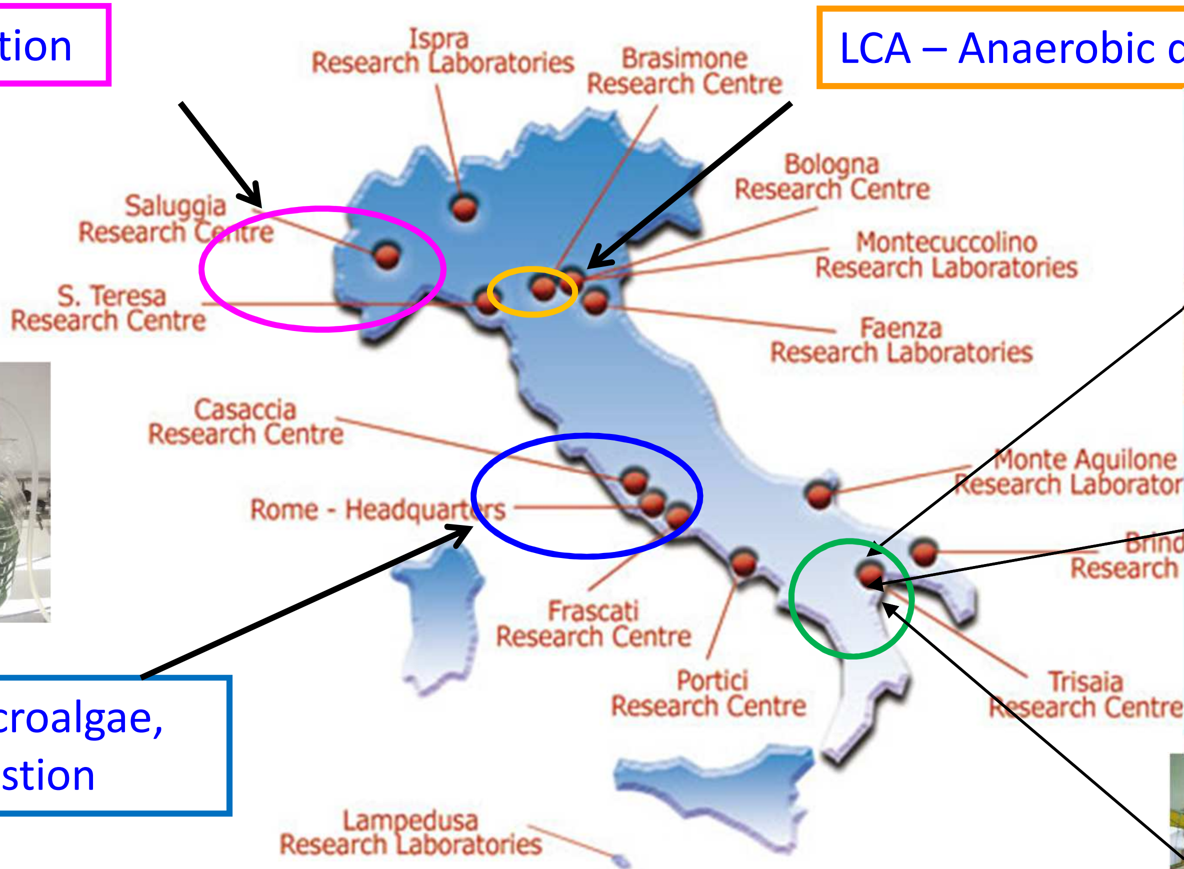
Isabella De Bari
ENEA CR TRISAIA, ITALY

IFIB 25-26 September 2014, Genova

ENEA'S RESEARCH CENTRES WITH ACTIVITIES IN THE BIOENERGY/BIOREFINERIES SECTOR

Biomass combustion

LCA – Anaerobic digestion



Biodiesel from microalgae, anaerobic digestion

ENEA TRISIAIA

Energy crops, thermochemical processes, biomass pretreatment and fractionation, biotechnological processes

INTERNATIONAL MEMBERSHIPS AND PARTNERSHIPS

- *Member of the Italian and European **technological platforms** on biofuels*
- *Member of the **Biobased-based Industries** Initiative (BBI)*
- *Member of the Italian cluster on the green chemistry (**SPRING**)*
- *Member of the **IEA bioenergy** tasks 33 on the gasification and 42 on bio refineries*
- *Founding member of **EERA** (European Energy Research Alliance)*

- *Government Agency for Cellulose and Paper, State Printing Office*
- *COMET Biorefining (Canada)*
- *CRF (FIAT Research institute)*
- *PCA (Pegeout)*
- *RENAULT(France)*
- *CNRS/IRC (France)*
- *QUB (Queen University of Belfast)*
- *UPAT (University of Patras)*
- *ECN (Netherlands)*
- *VTT (Finland)*
- *Lund University (Sweden)*
- *Risoe (Denmark)*
- *Nedalco (Holand)*
- *Roal (Holand)*
- *Budapest University*
- ***BIOCHEMTEX***
- ***NOVAMONT***
- ***VERSALIS***
- ....

RECENT

Lignocellulosics feedstocks

Lignocellulosic biomass = hardwood, softwood, herbaceous crops, agricultural straws, residues from forest thinning, etc.

The total potential of cellulosic wastes and residues in the EU ≈225 Mtonnes/yr

BIOMASS POTENTIAL IN ITALY AND AVAILABLE BIOMASS (energy in PJ)

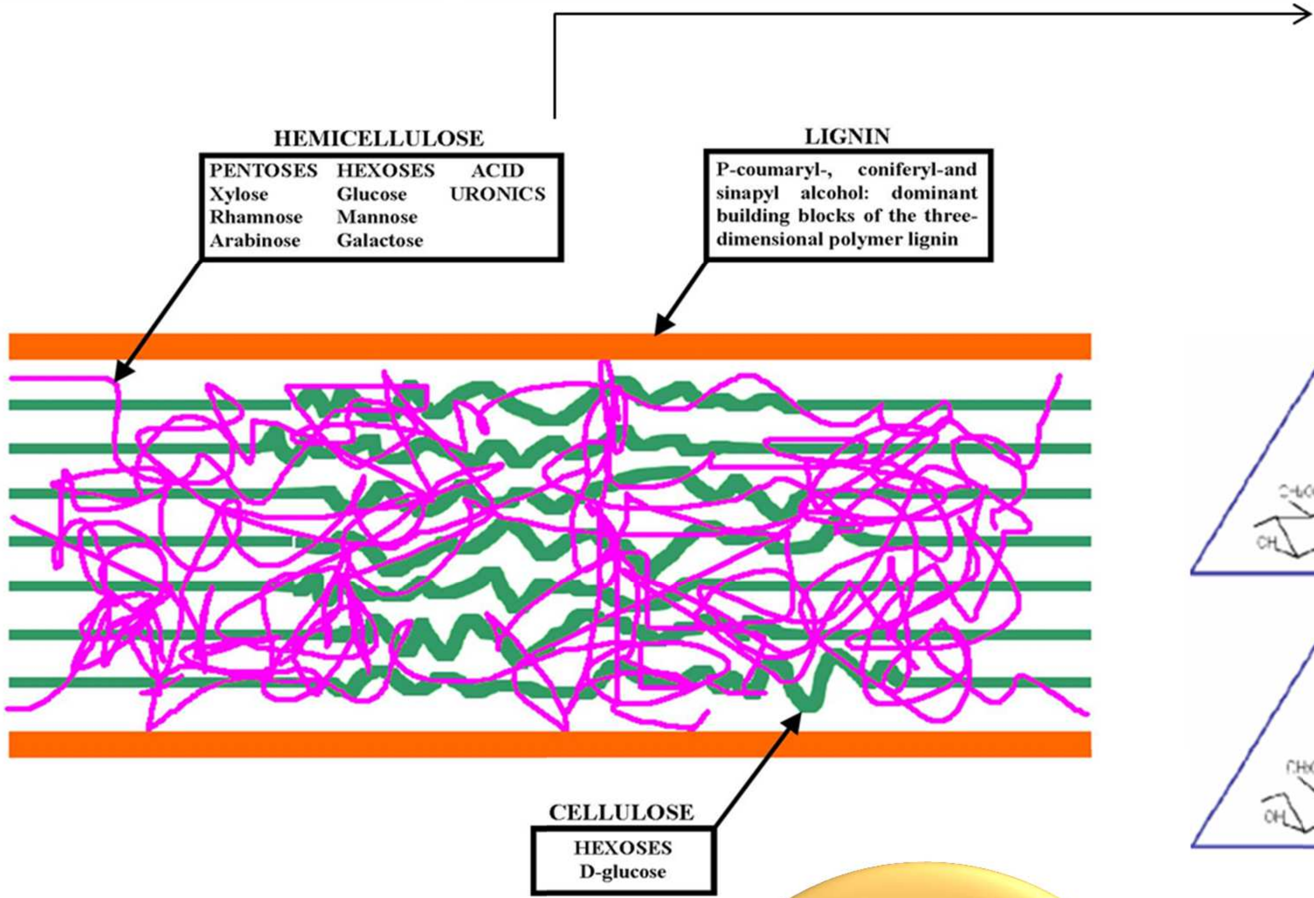
	[10]	[40]	[38]	[39]	[41]	[42]
Forestry	*167*	*38*	*180*	*247*	*121*	*544*
direct wood	167	38	138	176	100	448
indirect wood	0	0	38	71	21	96
Agriculture	*272*	*406*	*502*	*611*	*285*	*234*
crops	67	406	373	188	13	4
by-products	205	0	130	423	272	230
Waste	*100*	*25*	*113*	*201*	*176*	*67*
MSW	75	25	50	75	92	17
industrial	25	0	50	100	42	42
sewage sludge	0	0	13	25	8	8
Total	**540**	**469**	**783**	**1055**	**553**	**846**

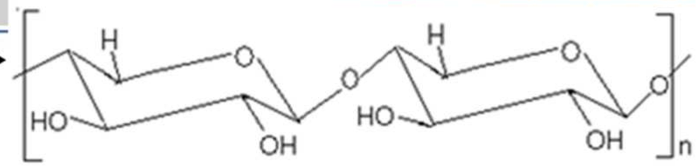
Source:
Renewable Energy 57 (2013) 448-461

National Renewable Energy Action Plans, 2011

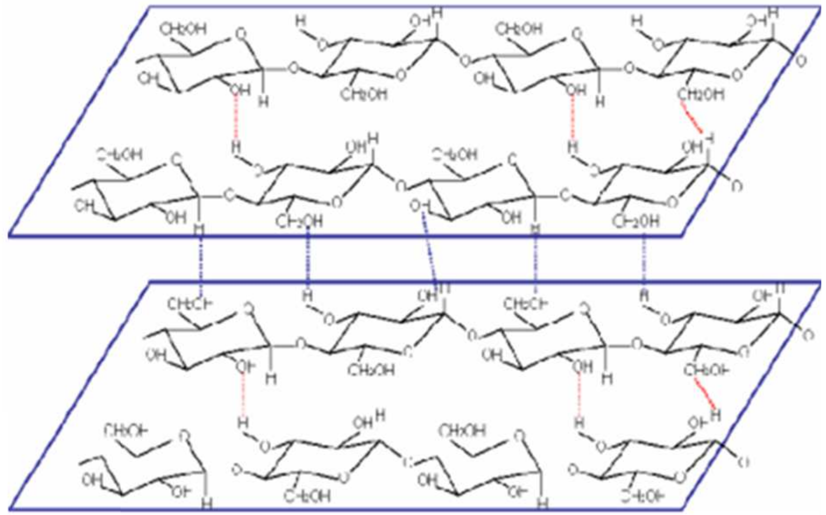
Data from the ENEA's ITALIAN BIOMASS ATALS

THE SUGARS PLATFORM





β(1→4)-D-xilopiranosio



SUGARS → BIOCHEMICAL AND/OR THERMOCHEMICAL ROUTE → CHEMICALS

BIOCHEMICAL ROUTE

FERMENTATION PRODUCTS	DETAILS	APPLICATIONS
ALCHOLS	Ethanol	ETBE, poly-ethylene
	Butanol	Fuels, chemicals
DIOLS	2,3-Butanediol, 1,4-Butandiol	Solvent, fuel, polymers/polyesters, fine chemicals
MICROBIAL LIPIDS	Tryacylglycerides	Fuel
ORGANIC ACIDS	Succinic a.	Tetrahydrofuran, 1,4 BDO, adipic acid, polyesters
	Itaconic a.	Polymers, resins, plastics,
	Lactic. A.	Lactides/PLA
TERPENOIDS	Farnesene	jet fuel component
POLYHYDROXYALKANOATES	Polyhydroxybutyrate	Polyesters, plastics
AMINO-ACIDS	Lysine	ε-caprolattame-> nylon 6
	Phenylalanina	styrene
	Aspartic acid	nylon 2,6

THE MAIN STEPS IN THE BIOCHEMICAL ROUTE

Process performances depends on:

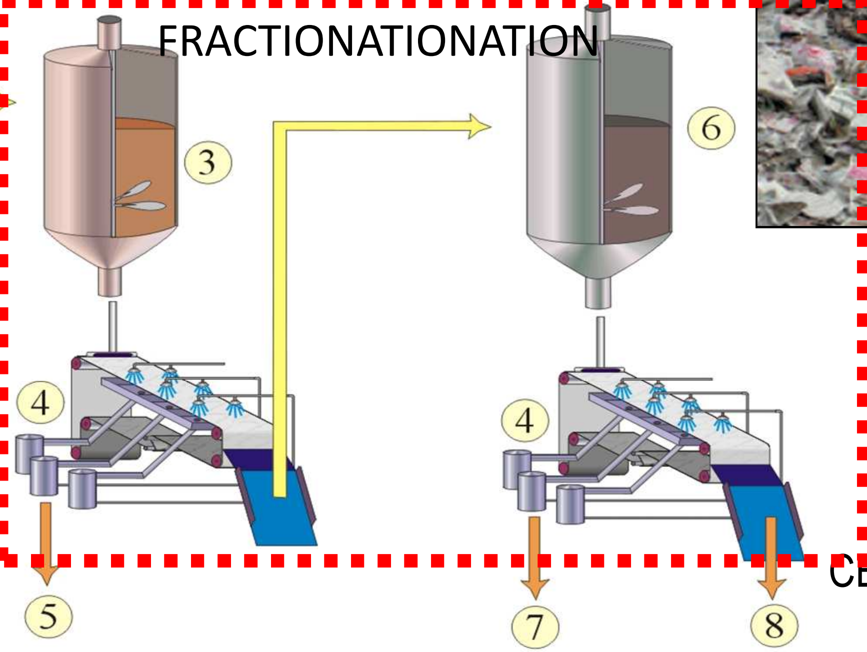
- Selection of effective pretreatment conditions
- Development of high gravity bioprocesses

BIOMASS PRETREATMENT AND FRACTIONATION

ENEA Steam Explosion Continuous Plant

PRETREATMENT

FRACTIONATIONATION



CELLULOSE

HEMICELLULOSE

LIGNIN

The biomass (1) is continuously steamed and exploded in the digester (2), then slurried with warm water (3) and filtered with a belt machinery (4) to recover hemicellulose (5). The residue is slurried with alcaline solution (6), then filtered to separate the lignin (7) from cellulose (8).

Cellulose:

1. **ethanol, butanol, lactic acid, BDO, green diesel, fatty alcohols**

2. : HMF, Levulinic acid

Lignin:

1. Energy
2. Aromatics

Hemicellulose:

1. Ethanol
2. polyols

2. Furans

FERMENTATION PRODUCTS

PRODUCTS FROM CHEMICAL CONVERSIONS

PRODUCTION OF CONCENTRATED SYRUPS

High gravity hydrolysis = process in which the solids content is above 20%

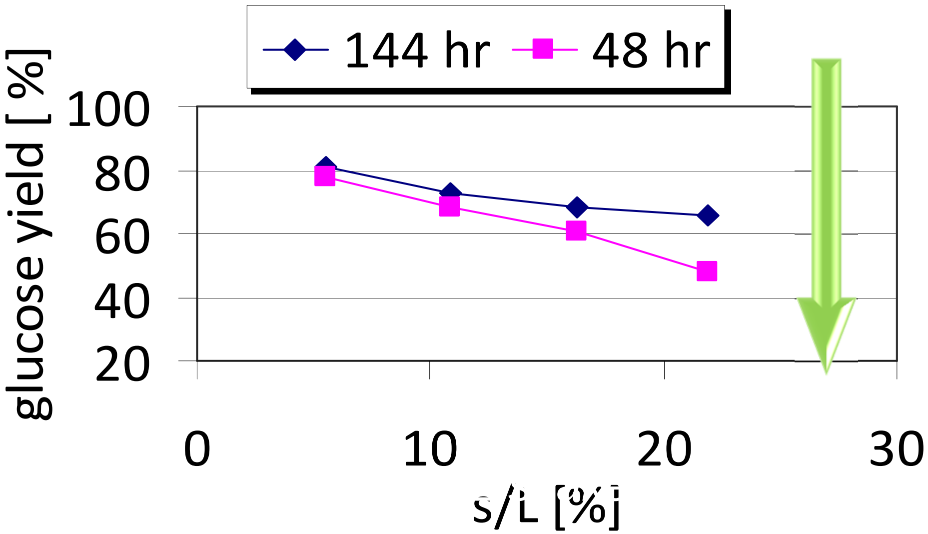
- Higher concentration of the final product
- Reduced downstream costs
- Reduced bioreactor capacity (→ lower installed costs)
- Lower amounts of waste waters

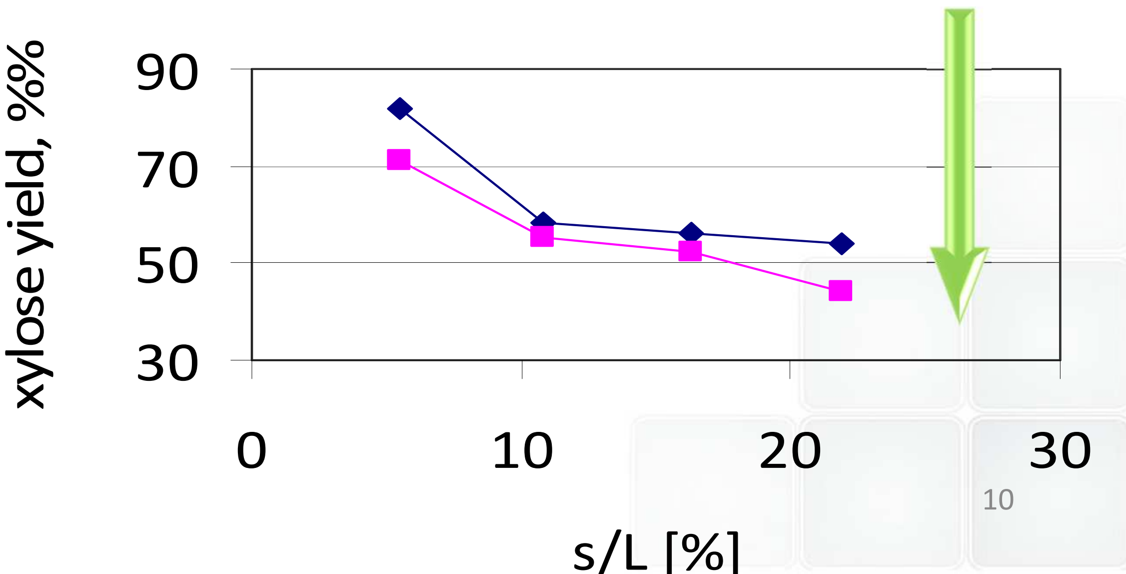
THE CHALLENGES

The Challenges of high gravity hydrolysis:
- ***High viscosities → mass transfer limitations → poor mixing***
- ***Inhibition by end-products***

The Challenges of high gravity fermentation:
- ***High concentration of microbial inhibitors***
- ***Osmotic stress due to high solutes concentration***
- ***Toxic effect of the product (synergistic inhibition)***

High gravity conditions reduce the process yields

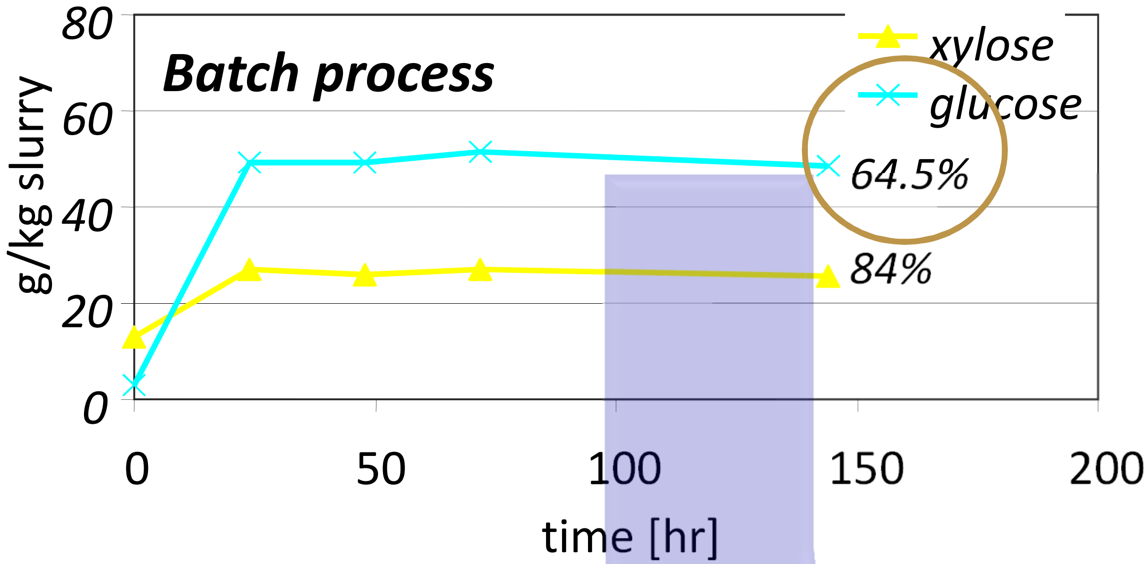




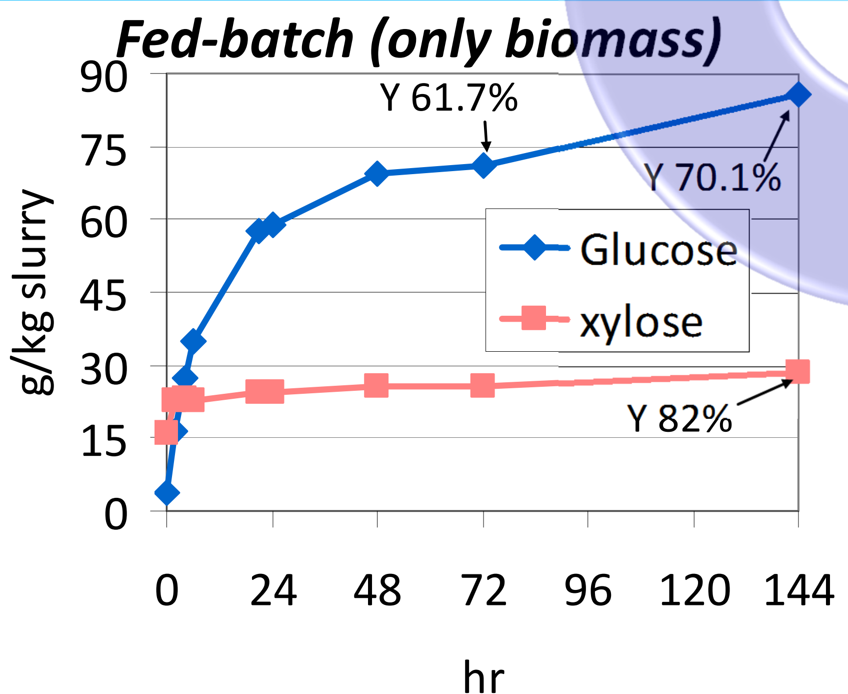
ENEA RESEARCH ACTIVITIES

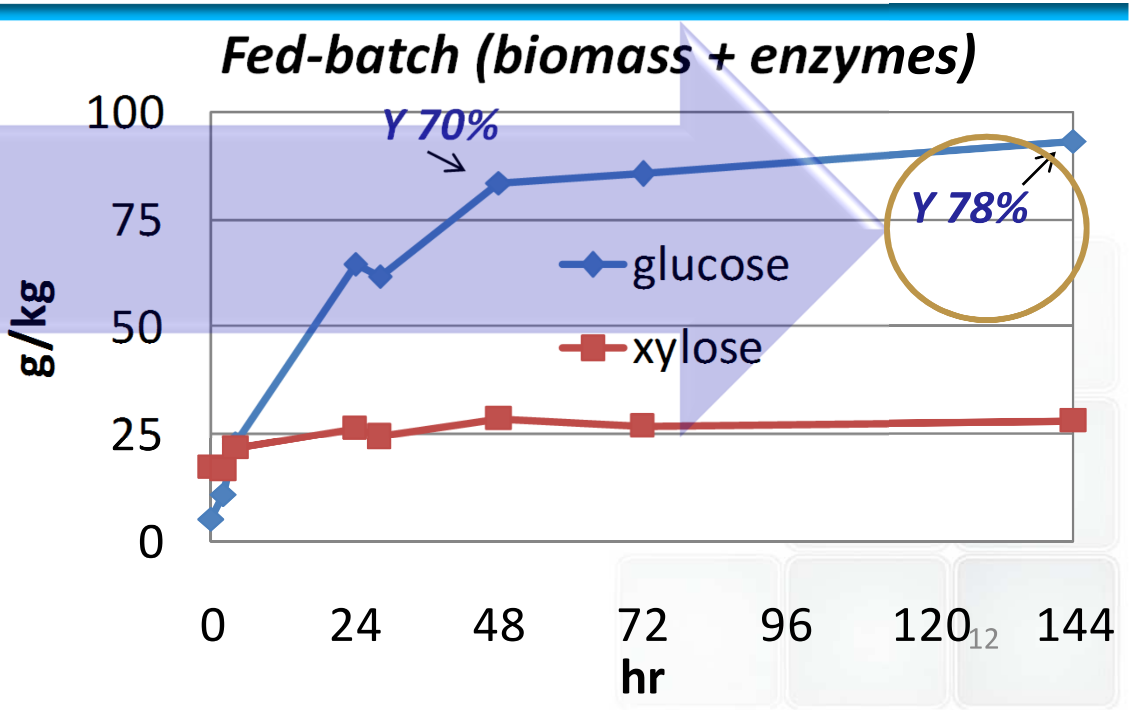
1. ***Optimize the enzymatic mix and the process conditions***
2. ***Optimize the bioreactors feeding strategies and reactor geometry/mixing***
3. ***Find the optimal process strategy (SSF, SHF, hybrid process)***
4. ***Develop robust fermentation processes***

OPTIMIZATION OF THE FEEDING STRATEGY



PROCESS STRATEGY+IMPROVED ENZYMATIC COCKTAIL



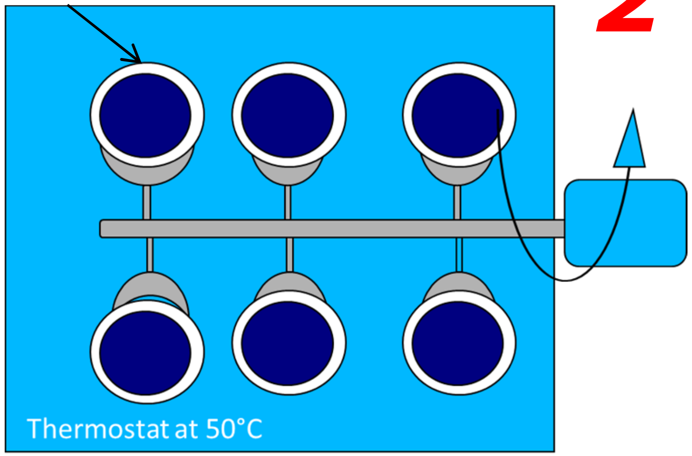


BIOREACTOR GEOMETRY

1

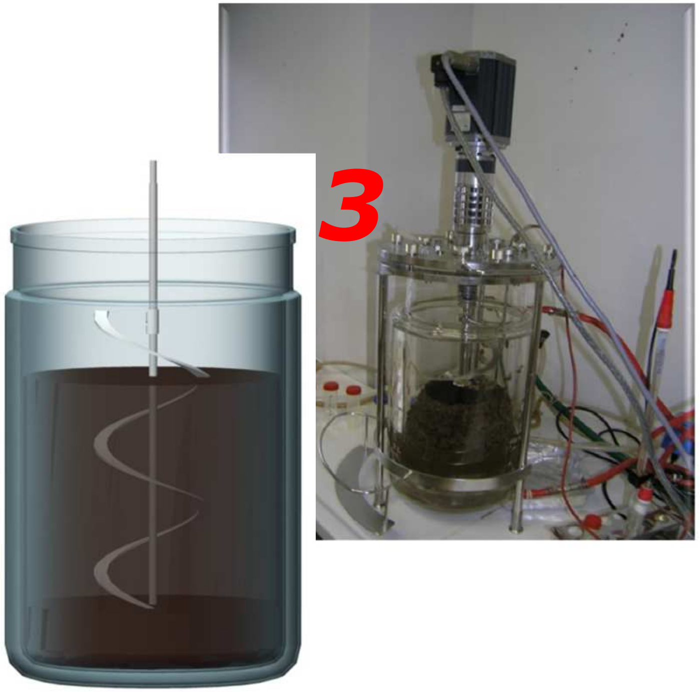
Shaking

flasks



2

Gravimetric mixing



3

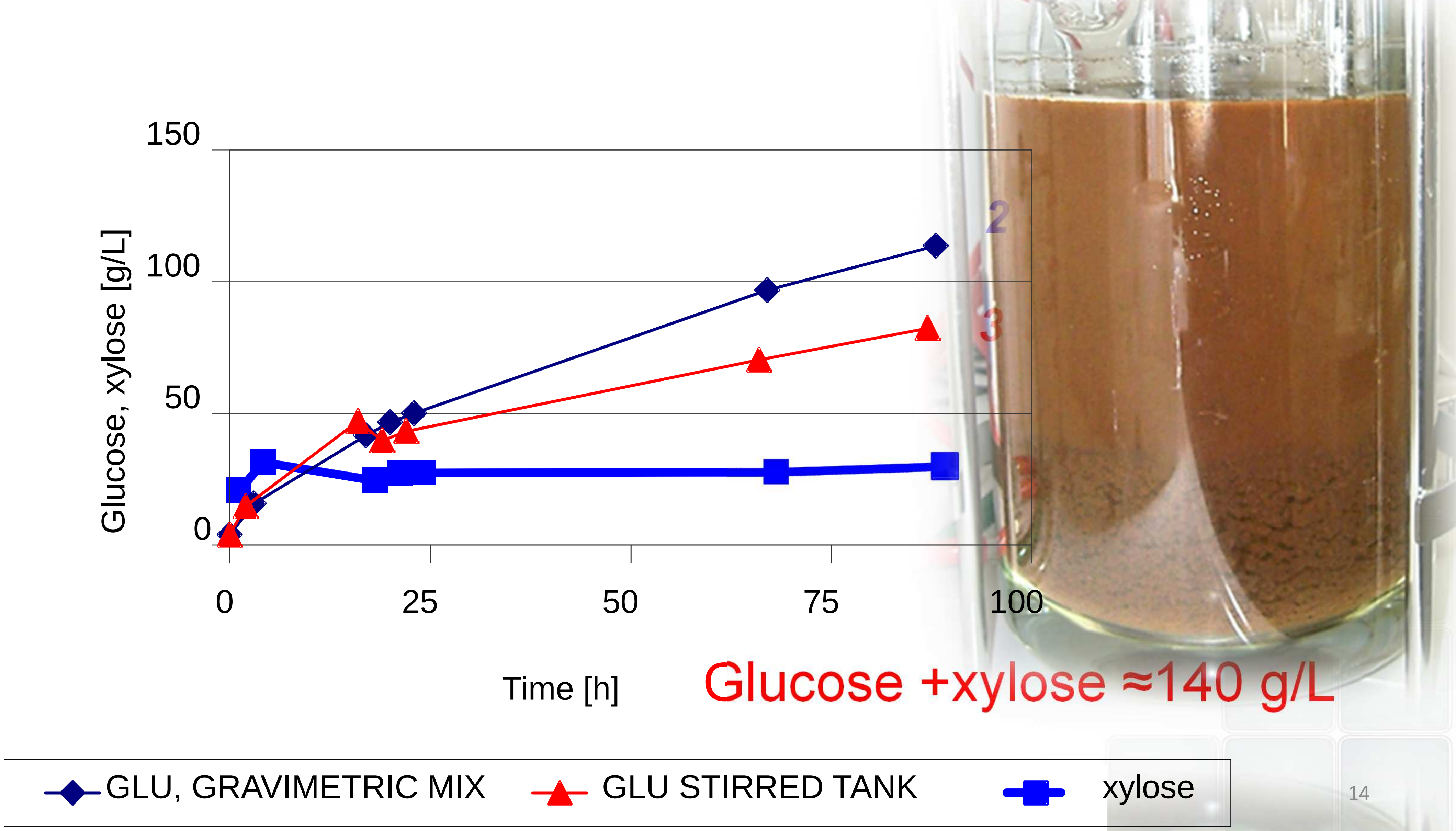
Stirring in vertical bioreactor

4

Stirring in horrizonatl bioreactor

EFFECT OF MIXING

Gravimetric shaking (2) was more effective than stirring in vertical bioreactor (3).



PRODUCTION OF CLEAN SUGARS

ENEA AGENZIA NAZIONALE PER LE NUOVE TECNOLOGIE, L'ENERGIA E LO SVILUPPO ECONOMICO SOSTENIBILE

Hydrolyzates detoxyfication is sometime necessary to increase the microbial conversion efficiency

Pretreated biomass/hydrolyzates

↓

Detoxification =rimoval of degradation by-products (i.e. organic acids, furan compounds, phenols)

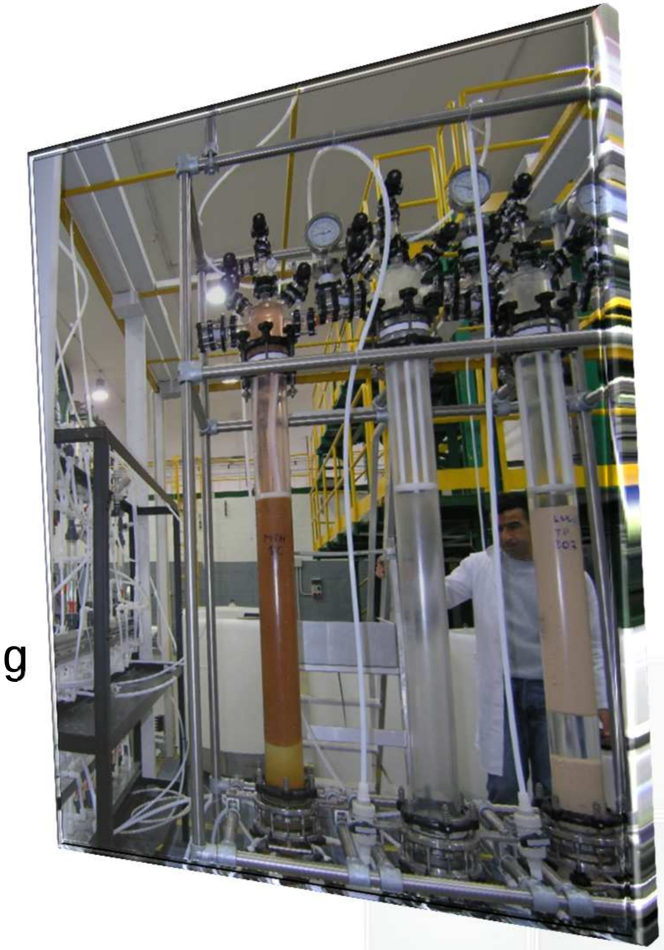
↓

ADAPTATION

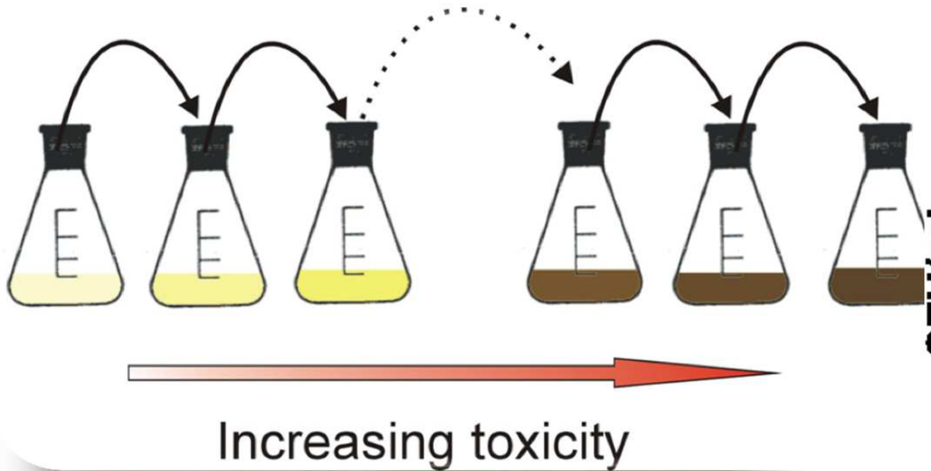
Fermentation

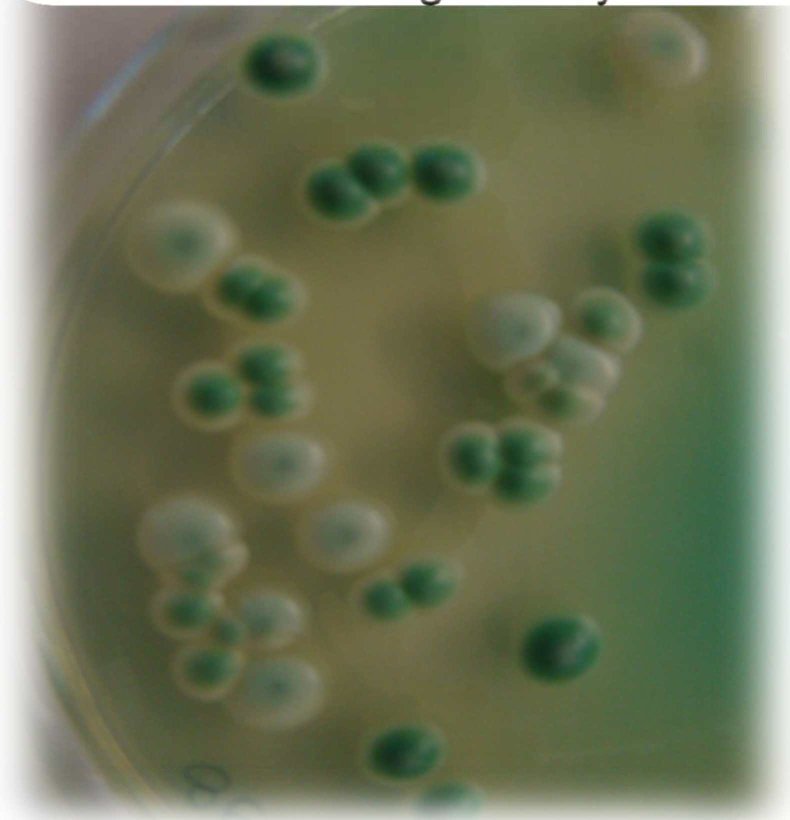
- Ion-exchange resins
- Overliming
- Steam stripping

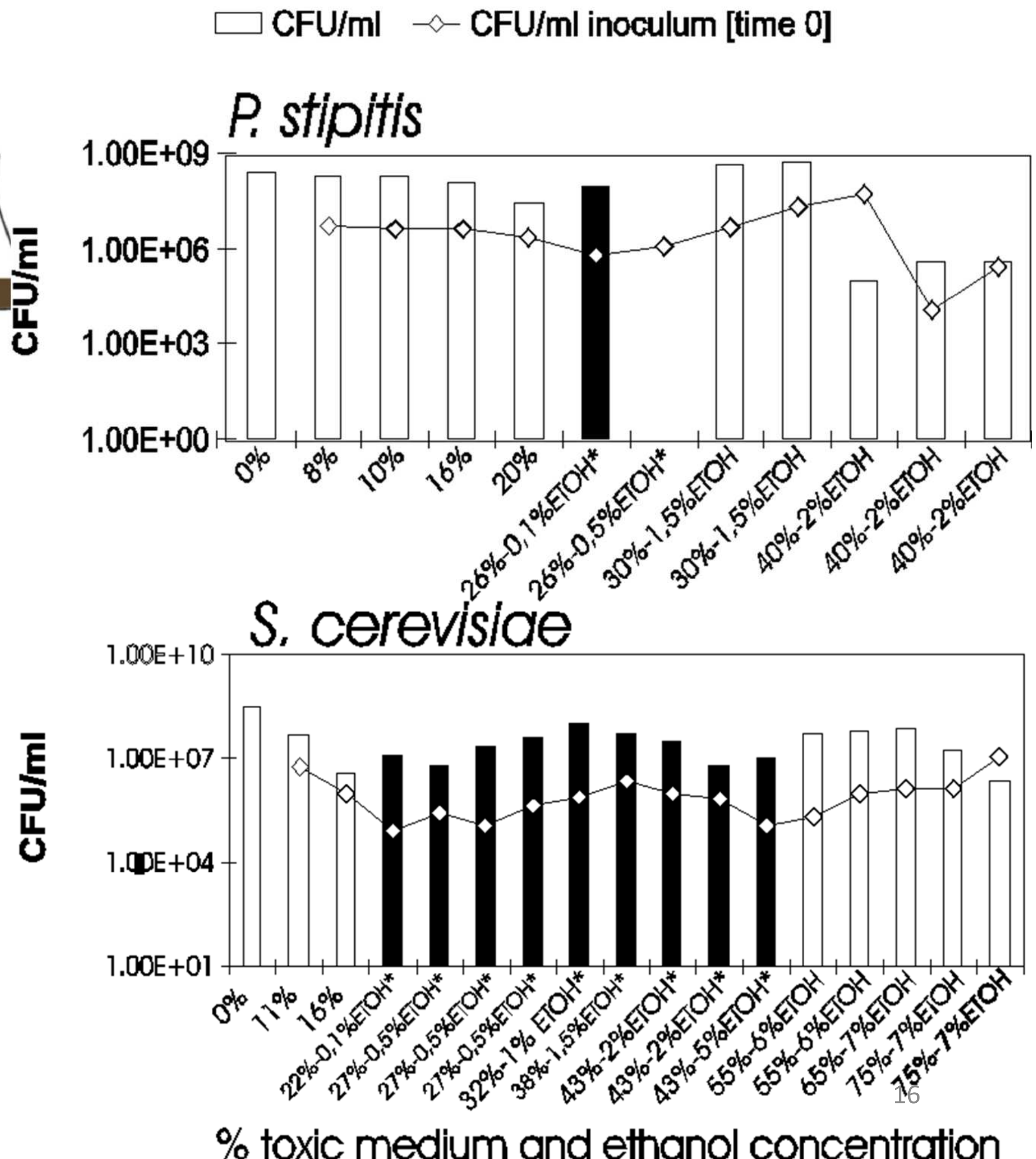
……………………..



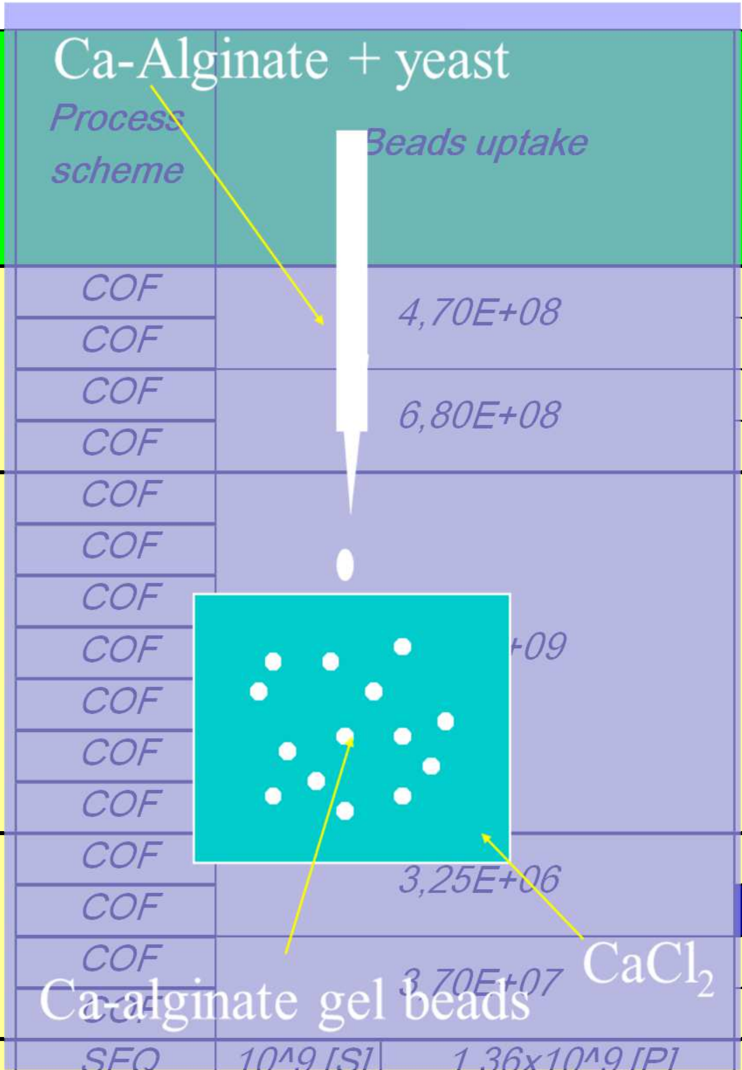
ROBUST MICROORGANISMS







FERMENTATION WITH ADAPTED MICROORGANIMS



Yeast(s) conditions	Process scheme	Beads uptake		P/S	% xylose consumption at maximum ethanol	% glucose consumption at ethanol maximum	Y%
WILD	COF	4,70E+08		4	16	100	68
	COF			4	16	100	66
	COF	6,80E+08		0,25	16	100	64
	COF			0,25	16	100	63
P. adapted up to 40%	COF	[illegible]+09		4	20	97	68
	COF				17	100	60
	COF				17	93	56
	COF				33	100	61
	COF				31	100	53
	COF				34	100	51
	COF				67	100	49
P. adapted up to 40% (repeated cycles)	COF	3,25E+06		4	34	100	72
	COF			4	42	100	80
	COF	3,70E+07		0,25	41	100	64
	COF			0,25	33	100	71
P. and S. adapted + EtOH	SEQ	10^9 [S]	1,36x10^9 [P]	4	73	100	61
	SEQ	10^9 [S]	5x10^9[P]	4	39	100	69

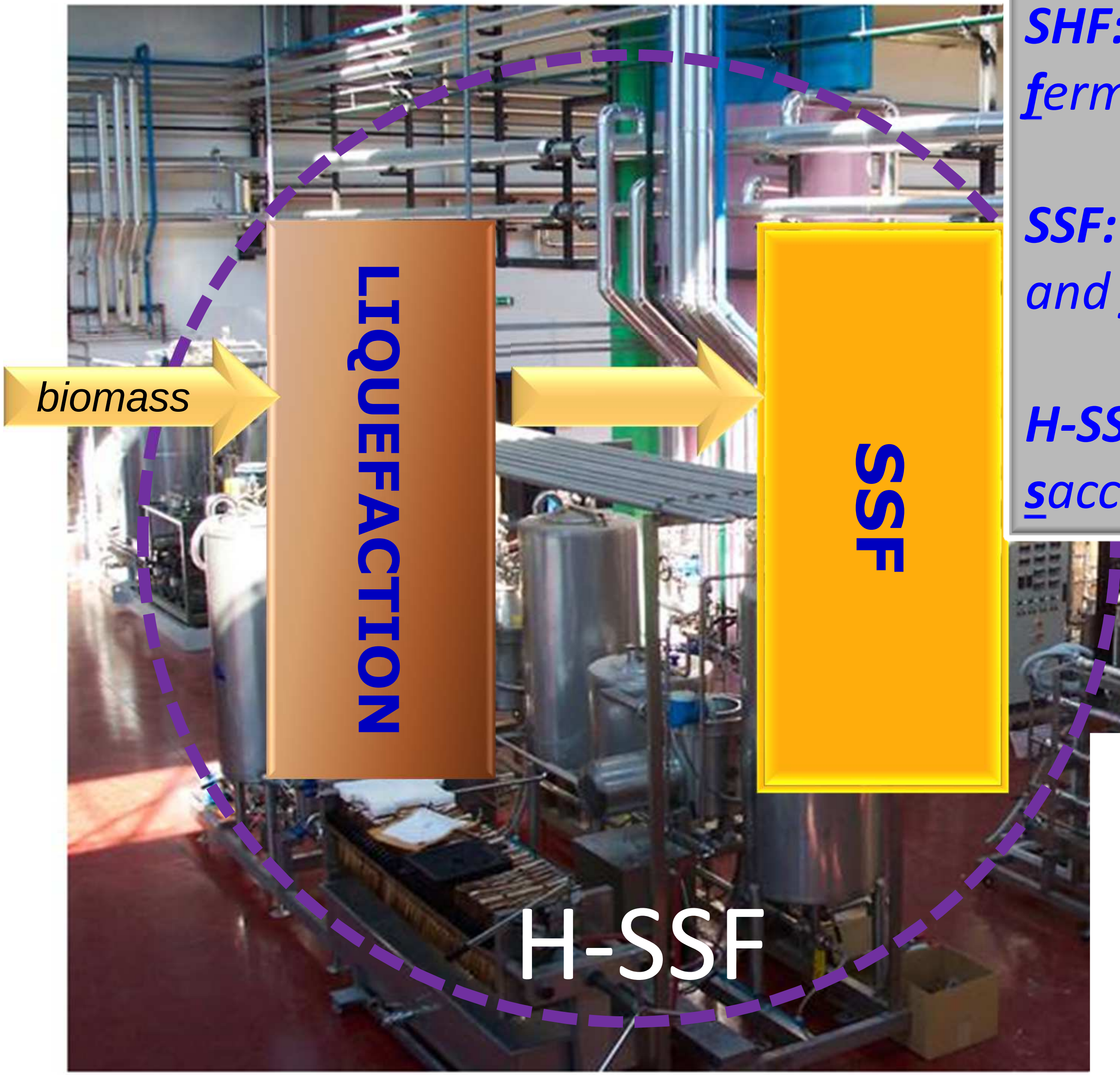
COF= cofermentation
SEQ= sequential fermentation

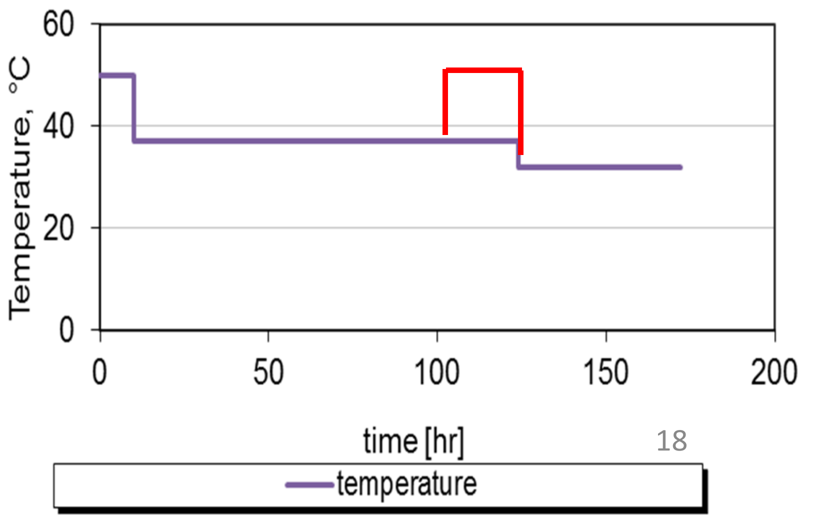
PROCESS OPTIMIZATION

SHF: <u>s</u>eparate <u>h</u>ydrolysis and <u>f</u>ermentation

SSF: <u>s</u>imultaneous <u>s</u>accharification and <u>f</u>ermentation

H-SSF : <u>h</u>ybrid <u>s</u>imultaneous <u>s</u>accharification and <u>f</u>ermentation





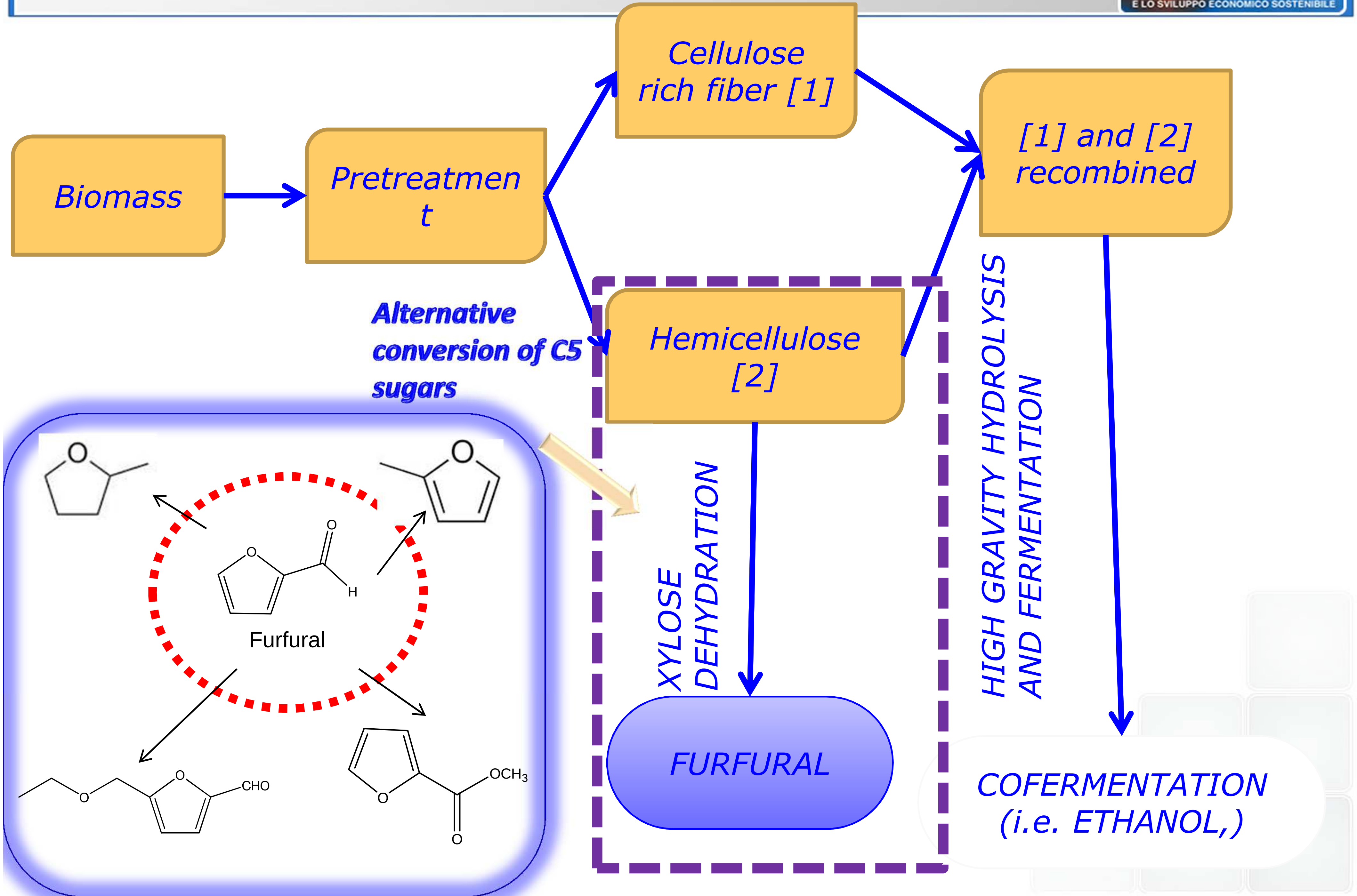
PRODUCTION OF BIOETHANOL

Enzyme dosage [g/g glucan]	Microrganisms	Process Type	Yeast inoculation	T [°C]	Ethanol (%wt)	Overall glucose [g/L]
0,22	*S. cerevisiae (M861)*	SHF	B	32°C	3,5	68
0,085	*S. cerevisiae (SIGMA II)*	HSSF	B	32°C	3,3	66
0,22	*K marxianus k6858*	H SSF	FB 1	32-50°C	1,4	74
0,085	*S. cerevisiae (SIGMA II)*	HSSF	FB 1	37-50°C	3,8	75
0,085	*S. cerevisiae (SIGMA II)*	HSSF	FB 3	37-50°C	3,8	75
0,085	*S. cerevisiae (SIGMA II)*	HSSF	B	37°C	3,7	75
0,22	*K marxianus k6858*	H SSF	B	32°C	1,6	77
0,22	*S. cerevisiae (SIGMA II)*	HSSF	FB 3	37-50°C	4,2	84
0,22	*K. marxianus k6271*	H SSF	B	32°C	4,4	85
0,22	*S. cerevisiae (SIGMA II)*	HSSF	B	37°C	4,2	90
0,22	*S. cerevisiae (SIGMA II)*	H SSF	B	32°C	4,6	91
0,22	*K. marxianus k6271*	H SSF	FB 2	32-50°C	4,7	91
0,22	*S. cerevisiae (M861)*	H SSF	B	32°C	4,8	92
0,22	*S. cerevisiae (M861)*	H SSF	FB 2	32-50°C	4,7	93
0,22	*S. cerevisiae (SIGMA II)*	H SSF	FB 2	32-50°C	5,0	98

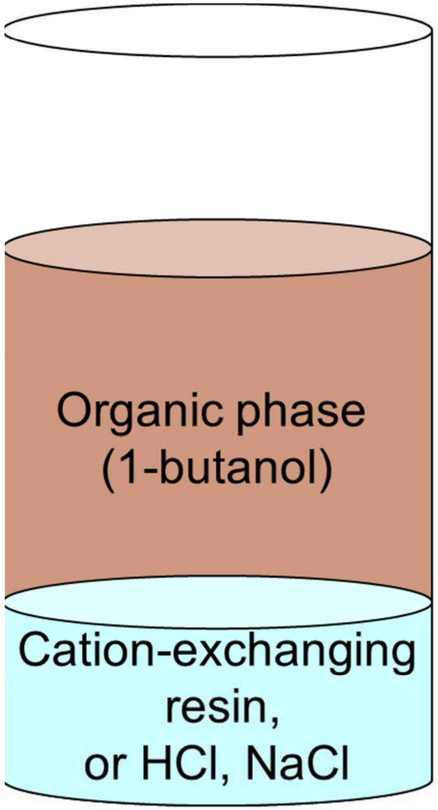
Reference

Glucose recovered

BIOREFINERY SCHEMES



MICROWAVES-ASSISTED DEHYDRATION OF SUGARS TO FURAN COMPOUNDS



- **The advantages of controlled microwave dehydration:**

Decreased reaction time and energy;

Reduced formation of secondary by products;

- **The advantages of the reactions in biphasic system:**

Extraction of the reaction product as it is formed;

Use of biomass derived solvent (butanol)

- **The advantages of using solid catalysts (resins, zeolites)**

Higher selectivity

DEHYDRATION OF XYLAN TO FURFURAL

process (min)	T °C	[H+]	Resin	Yield [g/$g_{SUBSTRATE}$] %	Sugar conversion %	selectivety
10	120		2,5	1,3	5	44
10	120		2	2,0	10	30
10	120		1,5	3,1	13	37
10	150	0,12		3,4	42	11
10	150	0,08		3,7	49	12
10	150	0,16		4,7	35	21
30	120		1,5	7,9	19	66
30	120		2	9,4	30	48
30	120		2,5	11,4	32	56
10	150	0,28		24,1	45	85
5	150		1,5	24,6	70	55
10	150		1,5	30,7	91	53
10	180	0,28		49,4	95	81

The process optimization requires the design of efficient catalysts

CONCLUSIONS

- The success of the various biorefineries concepts also depends on the development of (energetically) efficient processes which use limited amounts of chemicals/solvents, low catalysts dosages and catalyst recovery.

- ENEA is actively working on the development of green technologies and processes.

- A number of technologies and processes are available for the production and conversion of sugars

- Technologies and know- how developed for biofuels can be used to support the development of novel biorefineries concepts

THANKS FOR THE ATTENTION

isabella.debari@enea.it
+39 0835974313