Agro-industrie Recherches et Développements

SURFACTANTS DERIVED FROM WHEAT BYPRODUCTS

Dr. Boris ESTRINE
Head of Green Chemistry Department
b.estrine@a-r-d.fr

Coopératives Céréalières :
CHAMPAGNE CEREALES
CHAMPAGNE COLLIGNY
COHESIS
COOPERATIVE AGRICOLE JUNIVILLE
COOPERATIVE AGRICOLE D'ESTERNAY
EMC2
NOURICIA
SCA DE SEZANNE

Pfeifer & Langen

CHAMTOR

Glucose processing plant

C.R.D.

Céréales R&D

S.R.D.

Sucre R&D

60 %

20 %

20 %

A.R.D.

Agro-industrie Recherches & Developpements

95 %

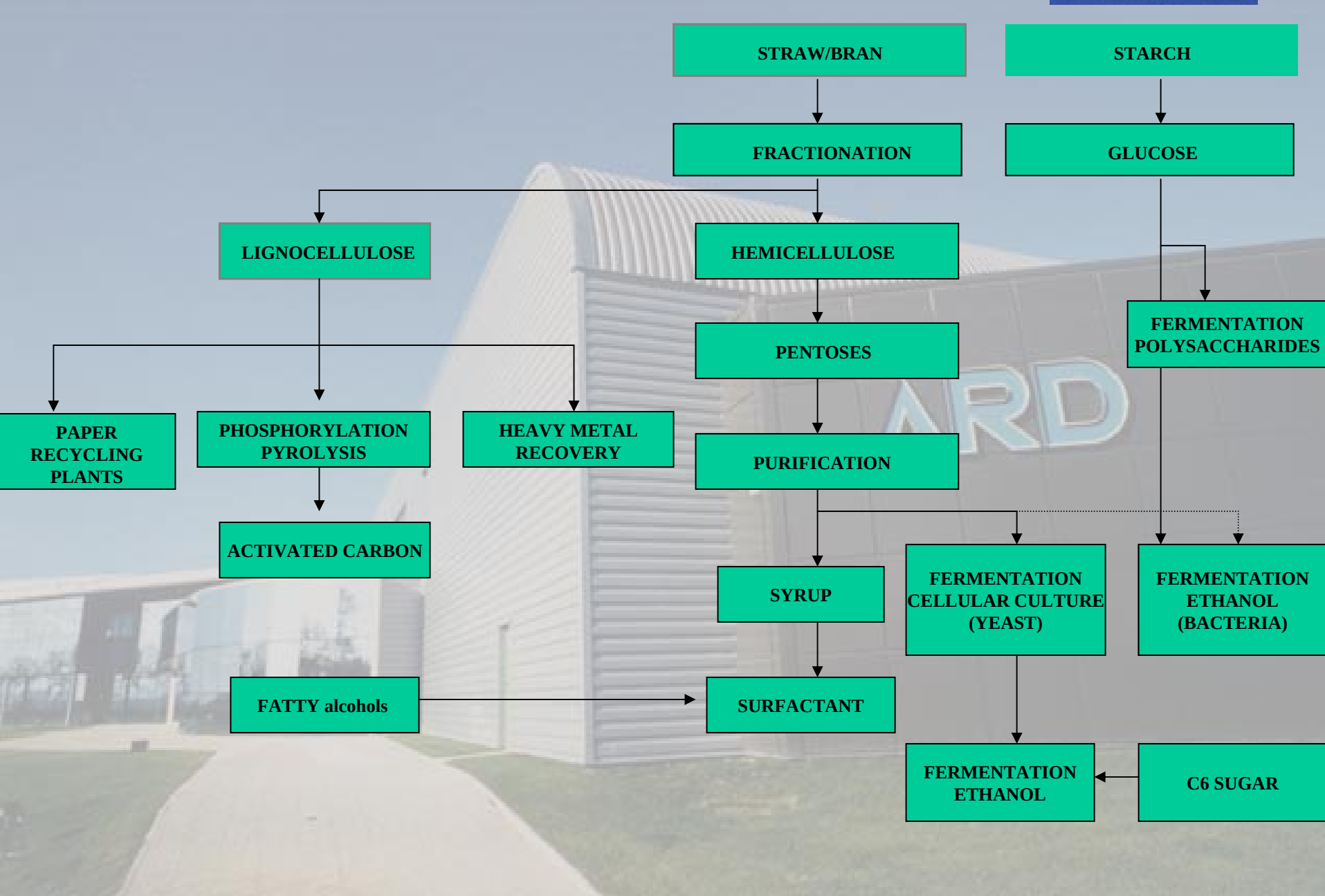
5 %

A.R.D. and SOLIANCE employees

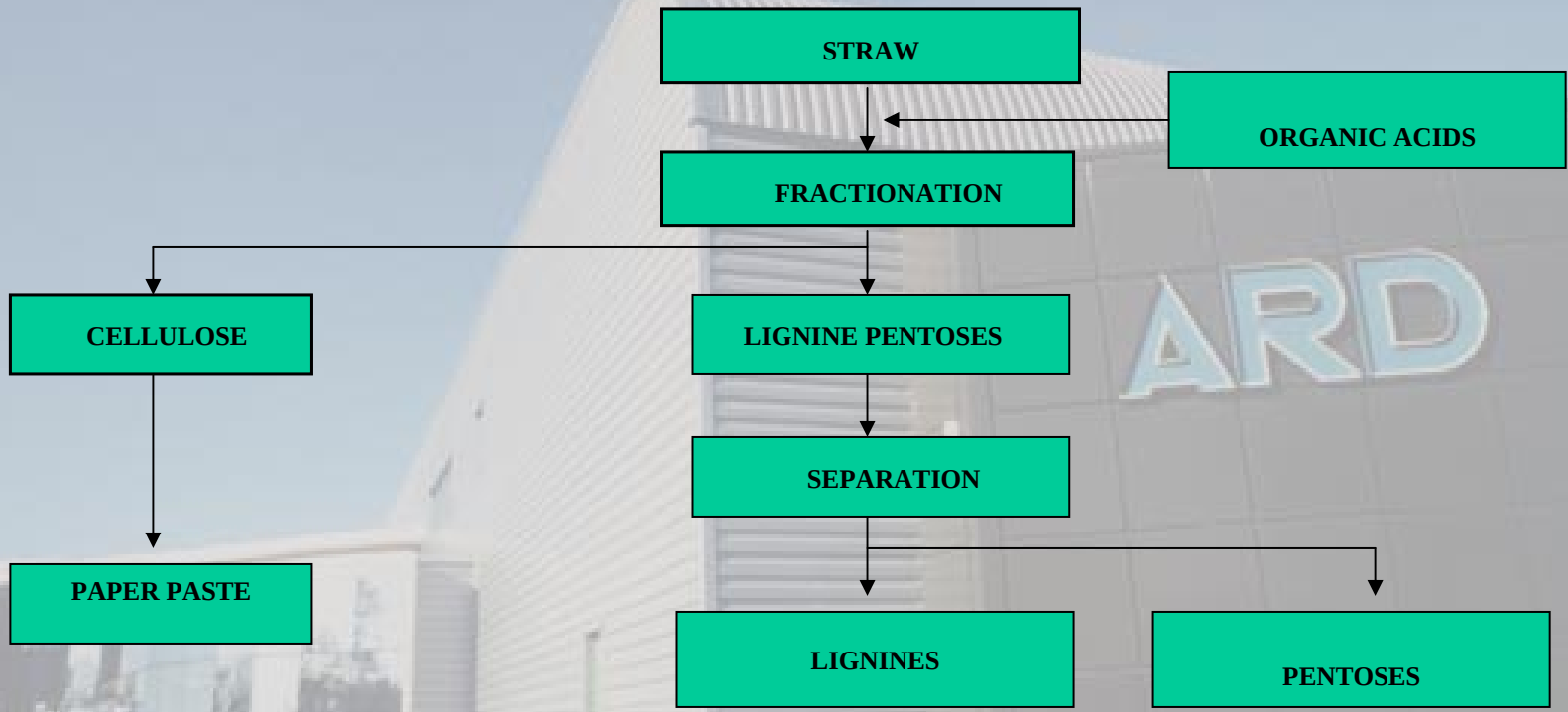
GROUPE SOLIANCE

Production of cosmetic ingredients

BIO REFINERY



ALTERNATIVE SCHEME



WHY ?

"Bio-products" from agricultural by-products

- Depletion of fossil resources / public consideration for environmental problems
- Need for farmers to envisage changes in European agricultural policy
- Agricultural co-products are available in high quantity and poorly valorised as foodstuff or cattle feed : farmers and agro-industrial firms ask for better added value
- Changes in regulatory affairs for chemicals (REACH)

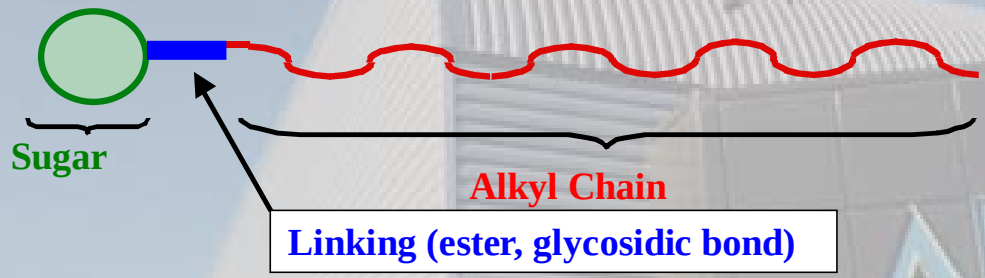
WHY ?

Surfactants from wheat by-products (bran and straw)

- global market volume size about 12 Mill. Tons (2003)
- non ionic surfactant represent around 40% of the market
- mostly used alkyl phenol E.O. : retired from the market for health considerations => place for low cost solutions and polyvalent surfactants (with low hazard and good environmental profile)
- solution of molecules derived from renewable agricultural resources
- agro-food industries generate by-products => biorefineries implemented in the same area
- availability : potential of 5 mill. Tons of sugars available from wheat by-products fractionation (only in France)

NOWADAYS :

carbohydrate based surfactants :



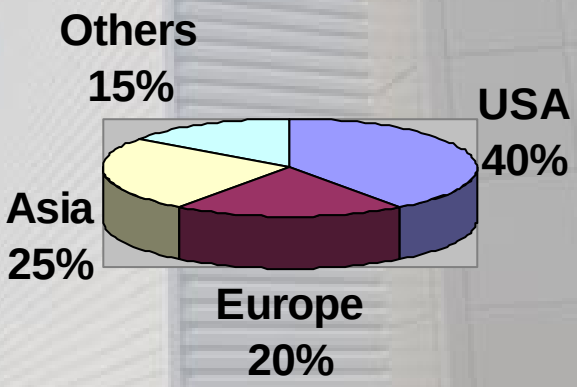
- sorbitan esters, sucrose esters, Me-Glu-esters, APGlu…
- sucrose: beet sugar, and glucose: corn or wheat starch =>low prices

Sugar	World production (t/year)	Price / kg
D-sucrose	113 614 000	0,31 €
D-glucose	5 000 000	0,60 €
D-sorbitol	650 000	0,90 €

NOWADAYS :

carbohydrate based surfactants :

World production of carbohydrate surfactants
(total : 200 000 t/year)



Only 200000 t/y in a possibility of 5 mill. T/y market volume size ?

1. **Price position : ex. APGlucosides (3-4 euros/kg) in comparison with the 1-2 euros/kg for EO alcohols**
2. **Performance and polyvalence!**

PRODUCTION OF SURFACTANTS FROM CEREAL CO-PRODUCTS BY GREEN CHEMISTRY

A·R·D

AGRO INDUSTRIE RECHERCHES ET DEVELOPPEMENTS

ARD PHILOSOPHY

Wheat Bran and Straw (around 40 euros/t)

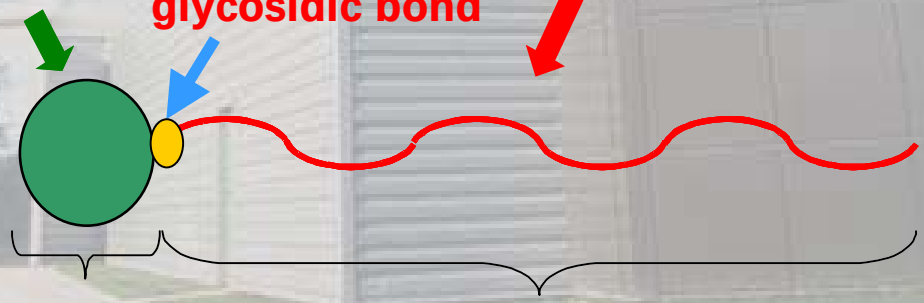
Xylose, Arabinose, Glucose

Plant oils :

Rapeseed, Palm, Coco, Coprah…

Hydrogenation of fatty acid to fatty alcohol

Link: glycosidic bond



Hydrophilic head

Lipophilic tail

PRODUCTION OF SURFACTANTS FROM CEREAL CO-PRODUCTS BY GREEN CHEMISTRY

A·R·D

AGRO INDUSTRIE RECHERCHES ET DEVELOPPEMENTS

Classical route for the preparation of APG

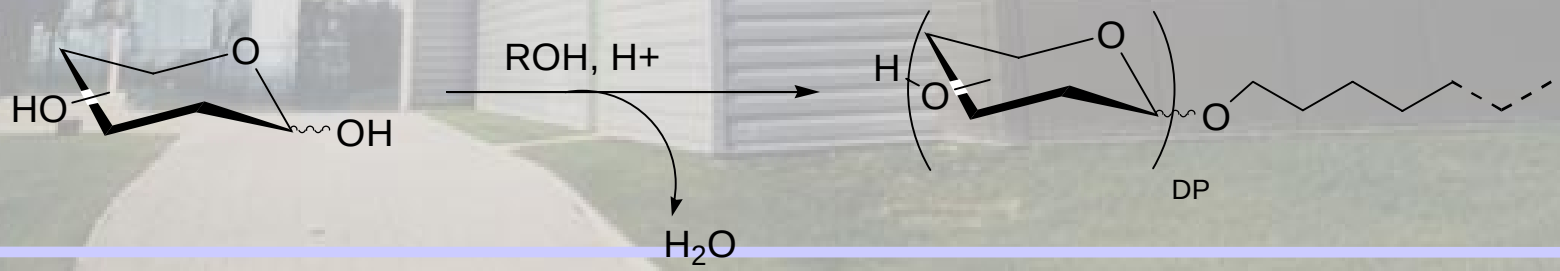
Corn or Wheat → Starch —*Hydrolysis*→ D-Glucose —*GLYCOSYLATION*→ APG

New approach developed by A.R.D. for new agro-surfactants

Wheat → Bran → Starch, Hemicelluloses —*Hydrolysis*→ D-Glucose, L-Arabinose, D-Xylose —*GLYCOSYLATION*→ New APG

Wheat → Straw → Hemicelluloses —*Hydrolysis*→ L-Arabinose, D-Xylose

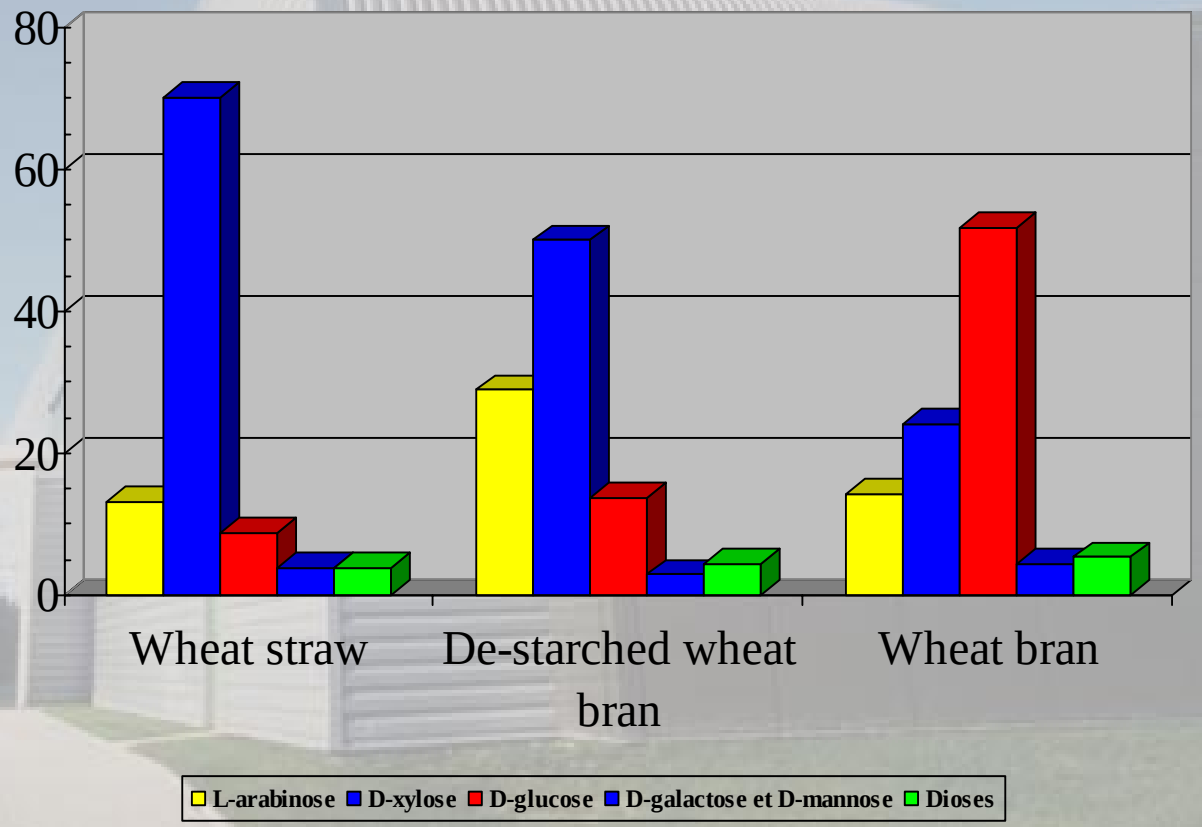
Green chemistry for green surfactants => free of solvent Glycosylation



PENTOSES FROM HEMICELLULOSES

Natural distribution of sugars : depending vegetable origin and process

Chromatography techniques allows easy separation and pure sugar manufacturing for tailored made surfactants



PRODUCTION OF SURFACTANTS FROM CEREAL CO-PRODUCTS BY GREEN CHEMISTRY

A·R·D

AGRO INDUSTRIE RECHERCHES ET DEVELOPPEMENTS

FRACTIONATION PROCESSES

Thermo-chemical	*Enzymic*
WHEAT BRAN	WHEAT BRAN
Washing	Washing
↓	↓
DESTARCHED BRAN	DESTARCHED BRAN
Acid hydrolysis at 130°C	Enzymic hydrolysis
↓	↓
BRAN HYDROLYSATE	BRAN HYDROLYSATE
Liming	Decantation & centrifugation
↓	↓
LIMED HYDROLYSATE	TROUBLE BRAN JUICE
Filtre-pressing	Ultrafiltration
↓	↓
NEUTRALISED JUICE	BRAN PERMEATE
Cationic & anionic exchange	Chromatography
↓	↓
DEMINERALISED JUICE	BRAN PENTOSE FRACTION
Concentration	Concentration
↓	↓
BRAN PENTOSE SYRUP	BRAN PENTOSE SYRUP

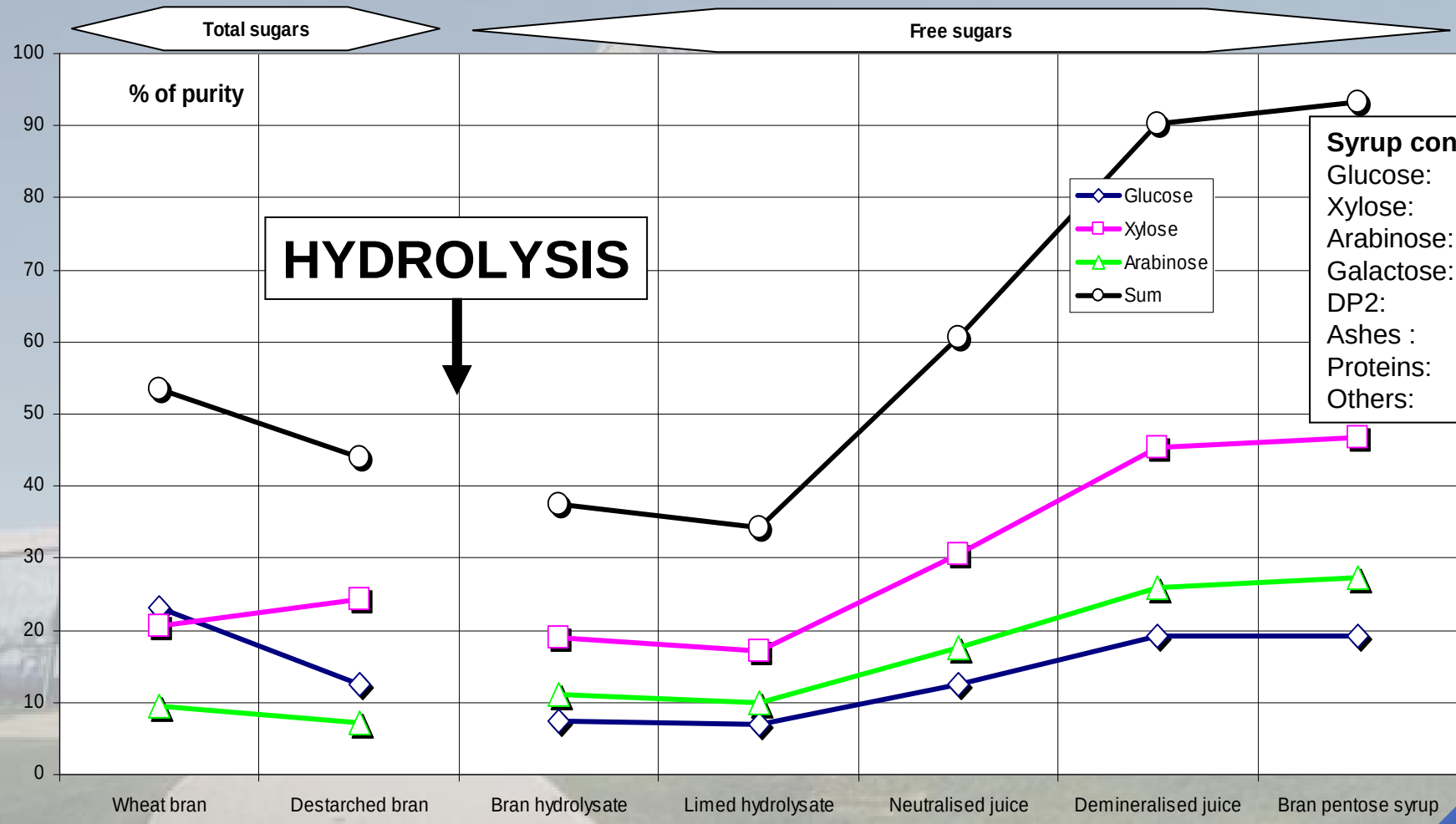
PRODUCTION OF SURFACTANTS FROM CEREAL CO-PRODUCTS BY GREEN CHEMISTRY

A·R·D

AGRO INDUSTRIE RECHERCHES ET DEVELOPPEMENTS

THERMOCHEMICAL PROCESS

Sugars evolution in processed bran



Syrup content

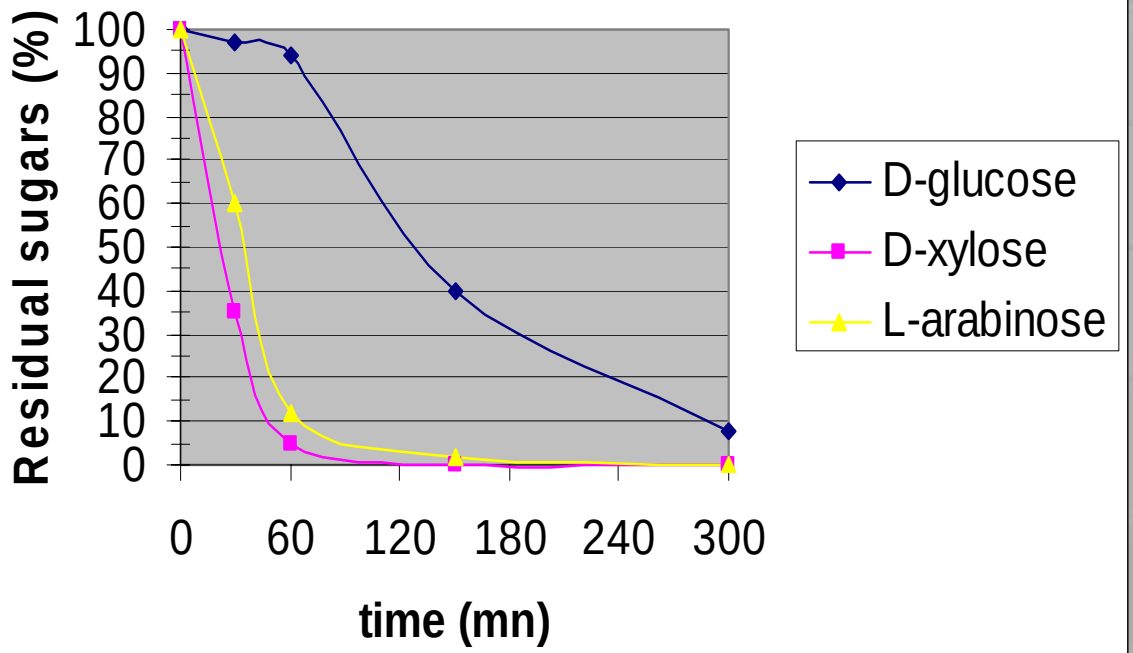
Glucose:	19%
Xylose:	47%
Arabinose:	27%
Galactose:	2%
DP2:	1,8%
Ashes :	0,2%
Proteins:	0,8%
Others:	1%

COMPARISON OF THE 2 PROCESSES

Treatment	T°C + Acid	Enzymes
Strength	High yield Very low DP amount	Specificity Cost of purification DP present
Weakness	Degradation products	Medium yield

ADVANTAGES OF BRAN SUGARS

Advantages in carrying out a sugars blend glycosidation :



1) pentoses show an higher chemical reactivity

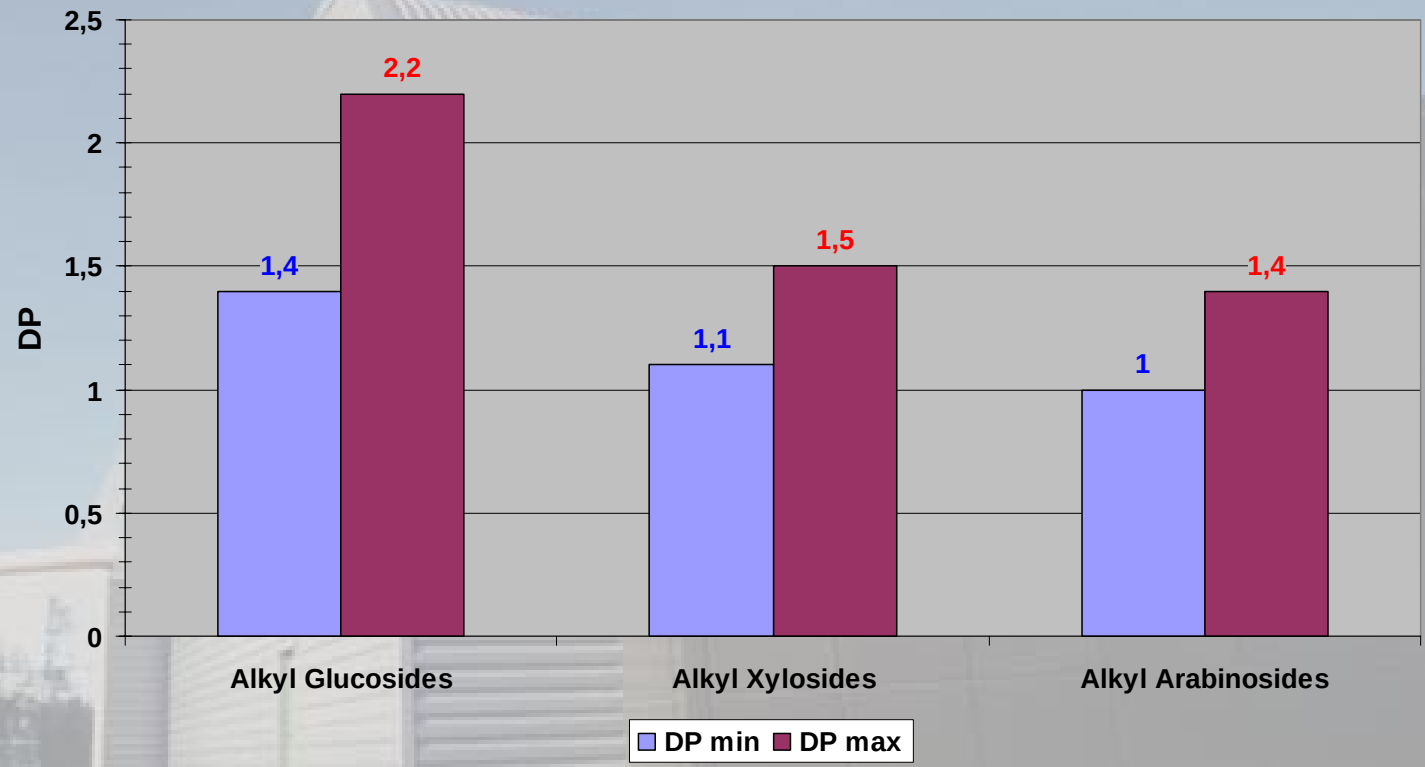
2) synergetic effect between pentoses and glucose, is increasing reaction kinetics

3) avoid sugars separation steps

4) grafting occurs below 120°C

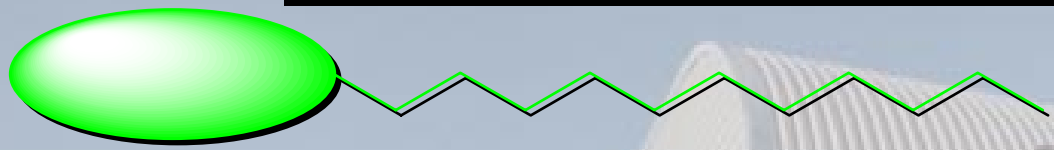
ADVANTAGES OF PENTOSES

Polymerization degree of alkyl glycosides

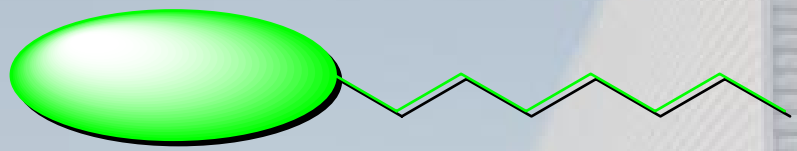


DP range is influencing the properties of surfactants ⇒ Large scale of properties (similar to surfactants derived from ethylene oxide)

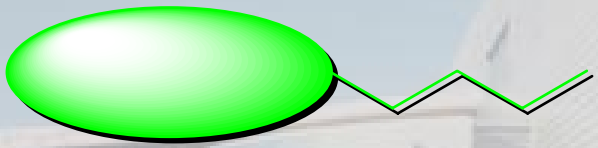
INFLUENCE OF FATTY ALCOHOLS Various length of fatty chain



14 to 22 carbons (Ex palm oil) → **Emulsifiers**



8 to 14 carbons (Ex palm kernel oil or coprah) → **Washing or foaming surfactants**



4 to 8 carbons (i.e. Fusel oil) → **Solubilizer, plasticizer, *etc.***

Mix of cleaning, foaming, detergent powers depending on the chain length and the compositions of sugar syrups.

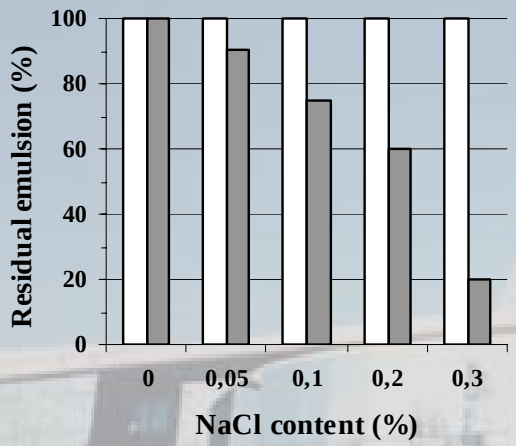
PRODUCTION OF SURFACTANTS FROM CEREAL CO-PRODUCTS BY GREEN CHEMISTRY

A·R·D

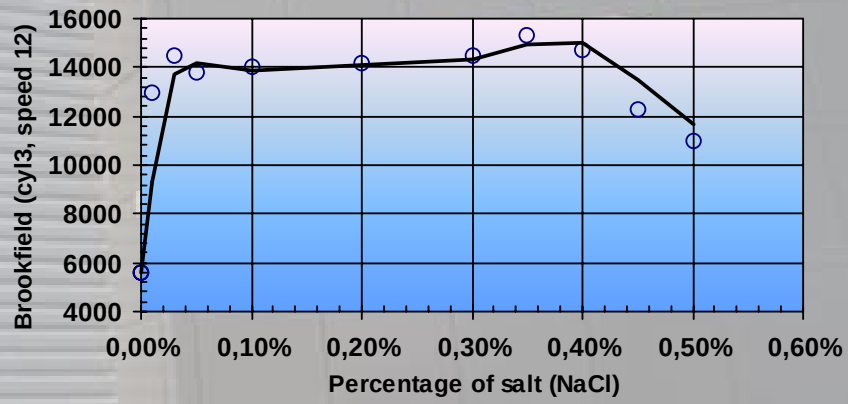
AGRO INDUSTRIE RECHERCHES ET DEVELOPPEMENTS

EMULSIFIERS: **Long tail APP for self emulsifying base: up to 47 % APG in starting alcohol (without distillation!)**
Non EO surfactant, no cloud point, low cost formulation

Neither thickener, nor co-emulsifier have been added for the test.



- Wheat Bran Glycosides
- Glycosides derived from glucose



Salts and pH stability > Classical Glucosides or EO Alcohols

Viscosity adjustments…

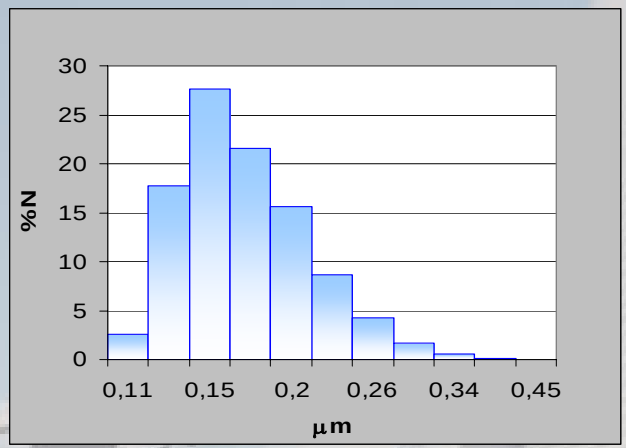
Applications: cream, milk for cosmetics / agrochemicals…

PRODUCTION OF NEW SURFACTANTS FROM CEREAL CO-PRODUCTS BY GREEN CHEMISTRY

A·R·D

AGRO INDUSTRIE RECHERCHES ET DEVELOPPEMENTS

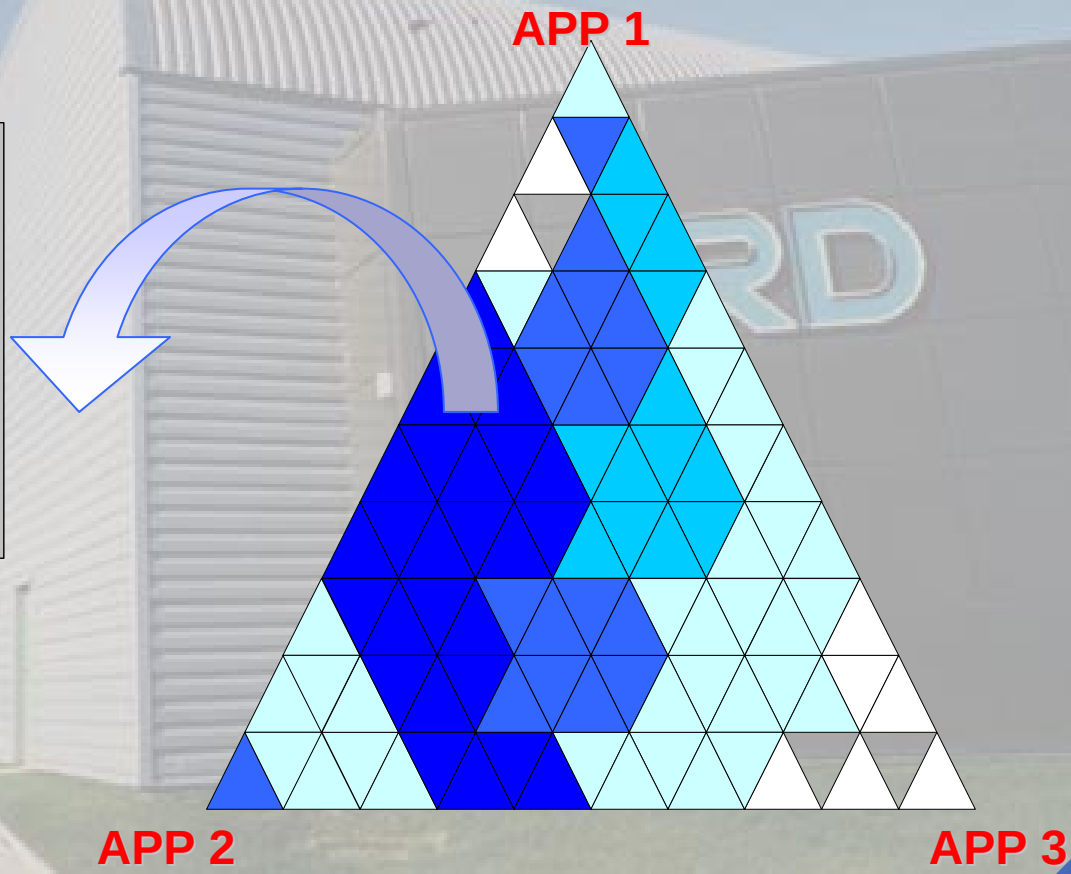
Liquid self emulsifying base: **Impossible with glucoside derivatives; the near-zero energy emulsification. Non EO surfactant for Mini-emulsions / Oily emulsifying concentrates / Sprayable emulsions for detergents/cosmetics and agrochemicals…**



$D_{[4,3]} = 0{,}2\ \mu m$

[0,5µm] emulsion area

Bluish emulsions



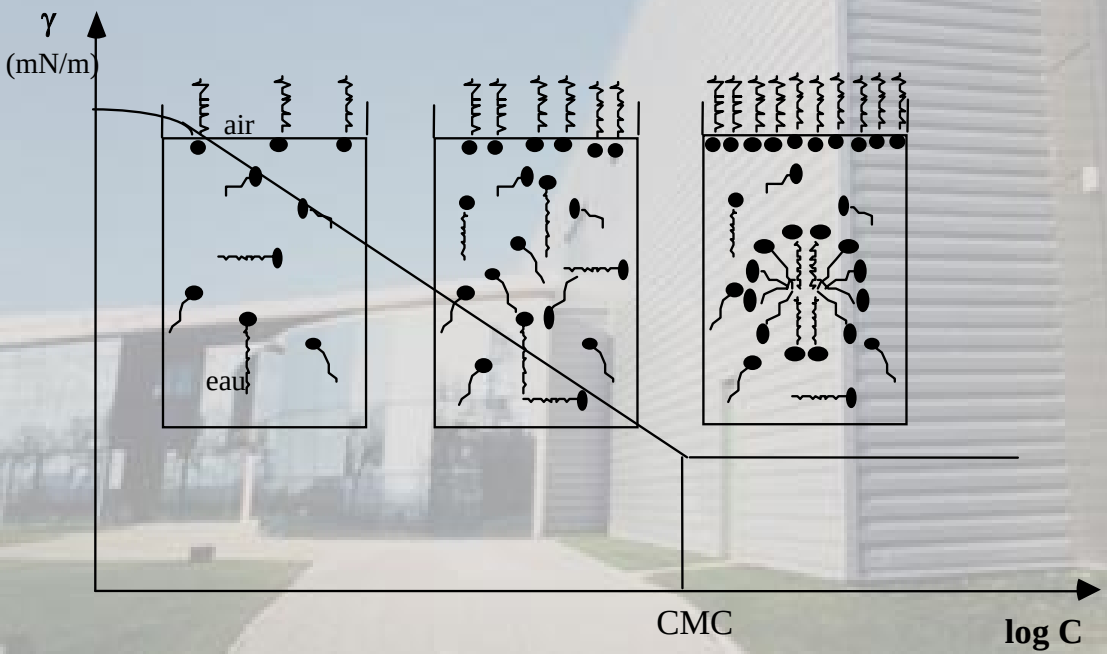
PRODUCTION OF NEW SURFACTANTS FROM CEREAL CO-PRODUCTS BY GREEN CHEMISTRY

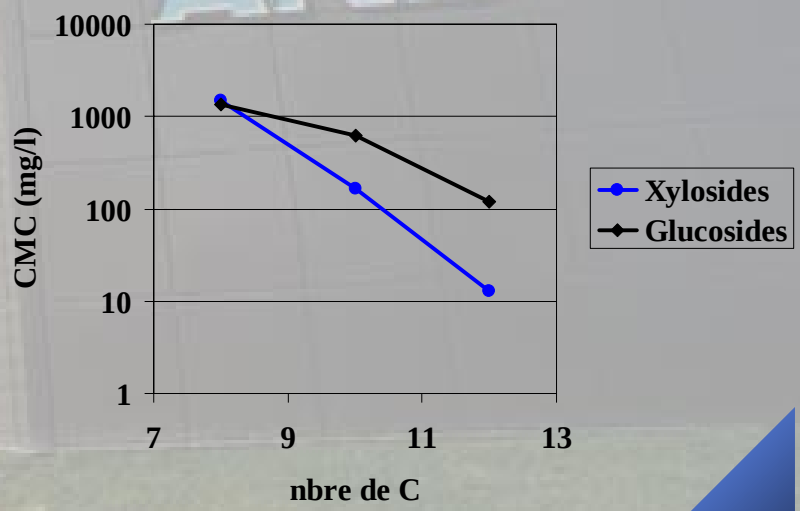
A·R·D

AGRO INDUSTRIE RECHERCHES ET DEVELOPPEMENTS

Foaming / Washing properties: Efficiency, Effectiveness of middle tail length APP for hard surface cleaning

- High micellisation speed
- Low surface tension: (γ_{CMC} = 25,5 à 27 mN/m)
- synergistic compatibilities





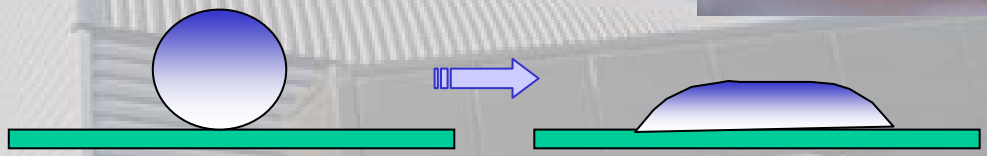
PRODUCTION OF NEW SURFACTANTS FROM CEREAL CO-PRODUCTS BY GREEN CHEMISTRY

A·R·D

AGRO INDUSTRIE RECHERCHES ET DEVELOPPEMENTS

***Wetting properties*:**

Highly effective detergents and agrochemicals



Reduction in the contact angles on hydrophobic surfaces

Contact angle (°)	Teflon	Paraffin
Water	104	96
APGlu	62	55
Pentosides	51	41

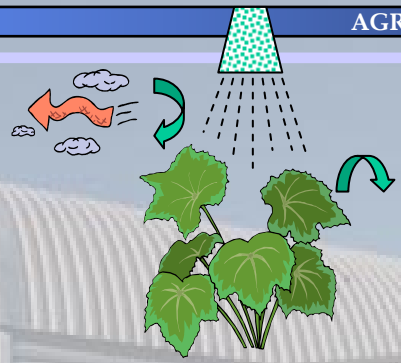
ARD Pentosides >> APglucoside

PRODUCTION OF NEW SURFACTANTS FROM CEREAL CO-PRODUCTS BY GREEN CHEMISTRY

A·R·D

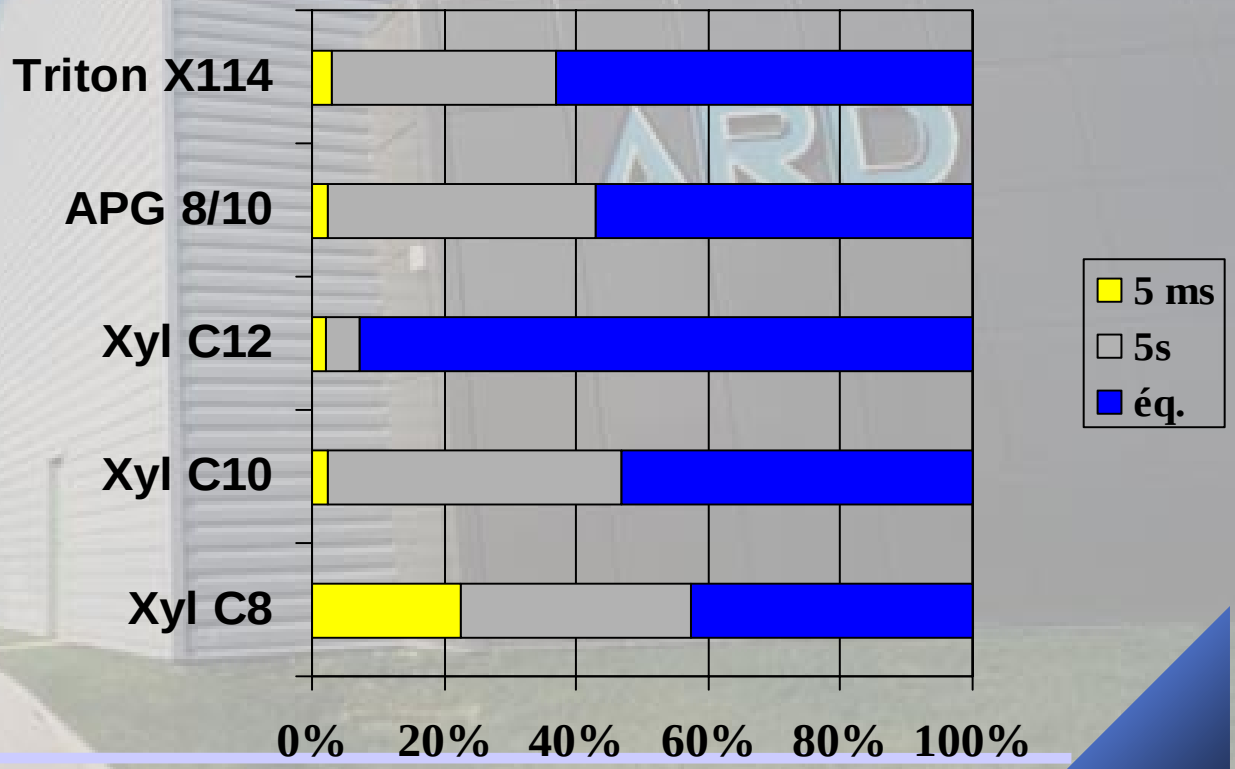
AGRO INDUSTRIE RECHERCHES ET DEVELOPPEMENTS

Drift under control :



Control size of the drops and avoids the rebounds

Efficiency of short middle to short tail pentosides



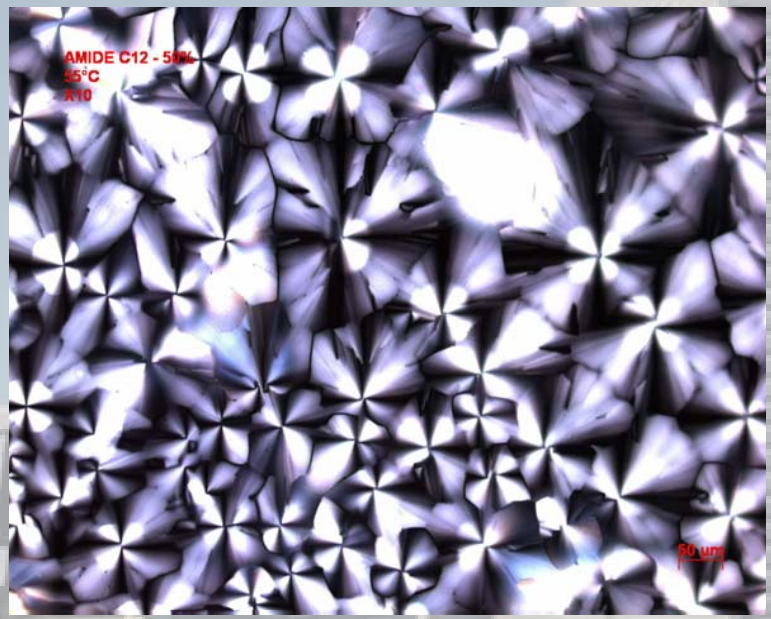
PRODUCTION OF NEW SURFACTANTS FROM CEREAL CO-PRODUCTS BY GREEN CHEMISTRY

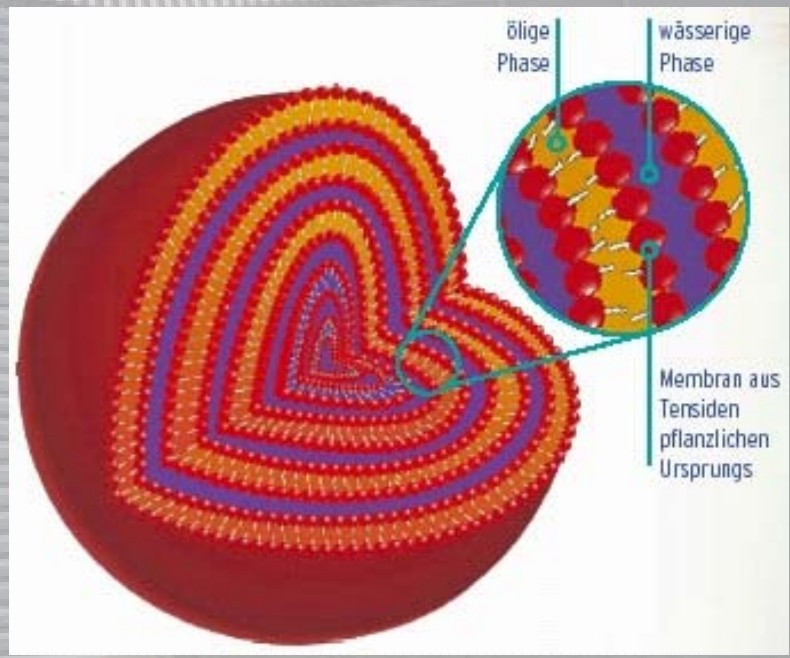
A·R·D

AGRO INDUSTRIE RECHERCHES ET DEVELOPPEMENTS

***Striking differences with APG in two phases diagrams*:**

Protection and control release of thermo-sensible cosmetics or phyto-ingredients



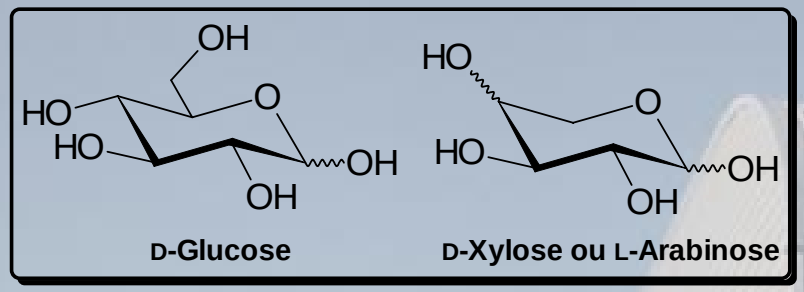


SPHERULITES

PRODUCTION OF NEW SURFACTANTS FROM CEREAL CO-PRODUCTS BY GREEN CHEMISTRY

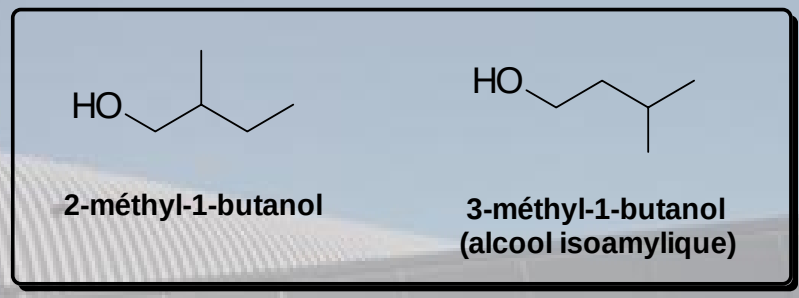
A·R·D

AGRO INDUSTRIE RECHERCHES ET DEVELOPPEMENTS



D-Glucose

D-Xylose ou L-Arabinose



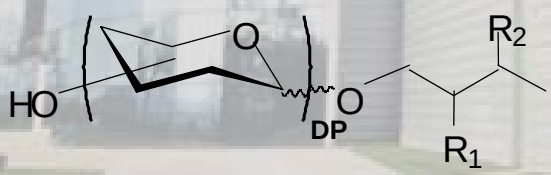
2-méthyl-1-butanol

3-méthyl-1-butanol
(alcool isoamylique)

Wheat bran & wheat straw
By-products of cereal industry

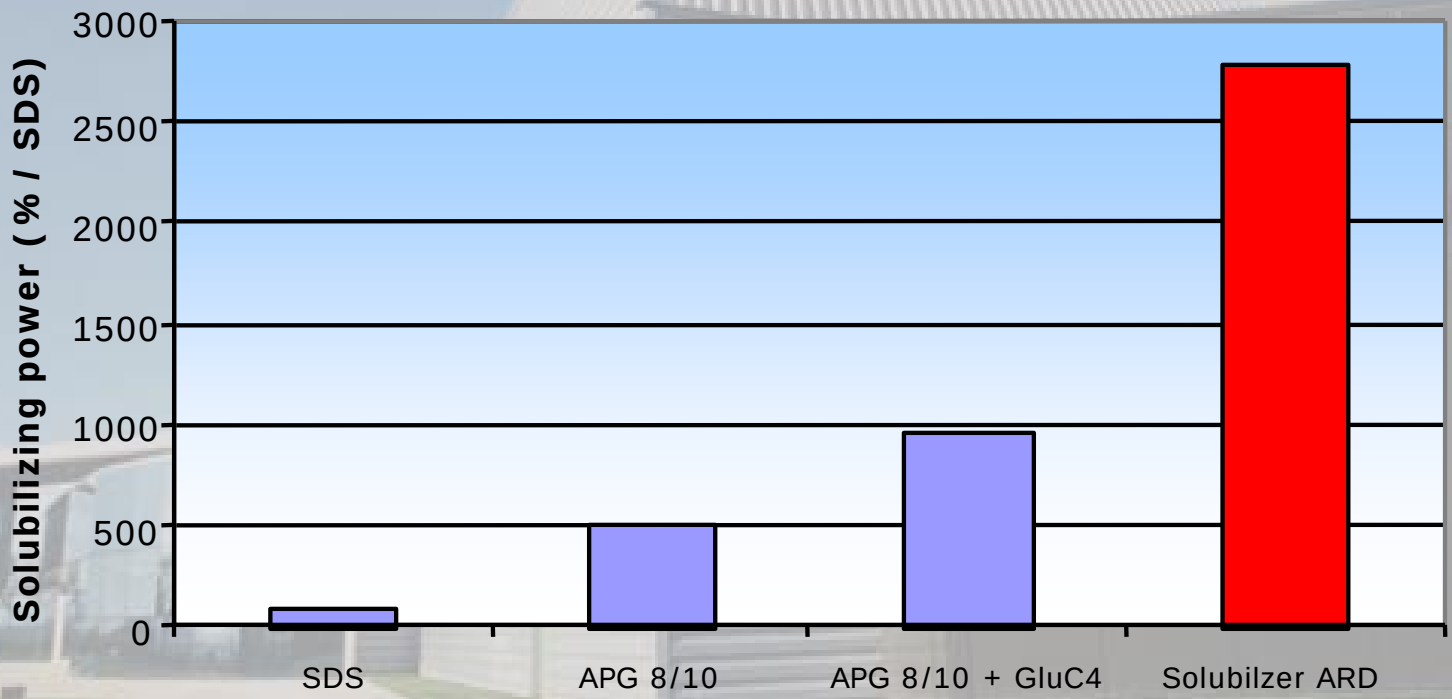
Fusel oil
By products of sugar (ethanol) industry

SOLUBILIZER : short tail APP



R_1=H , R_2=Me ou R_1=Me , R_2=H

Strong solubilizing power



Solubilization of perfumes

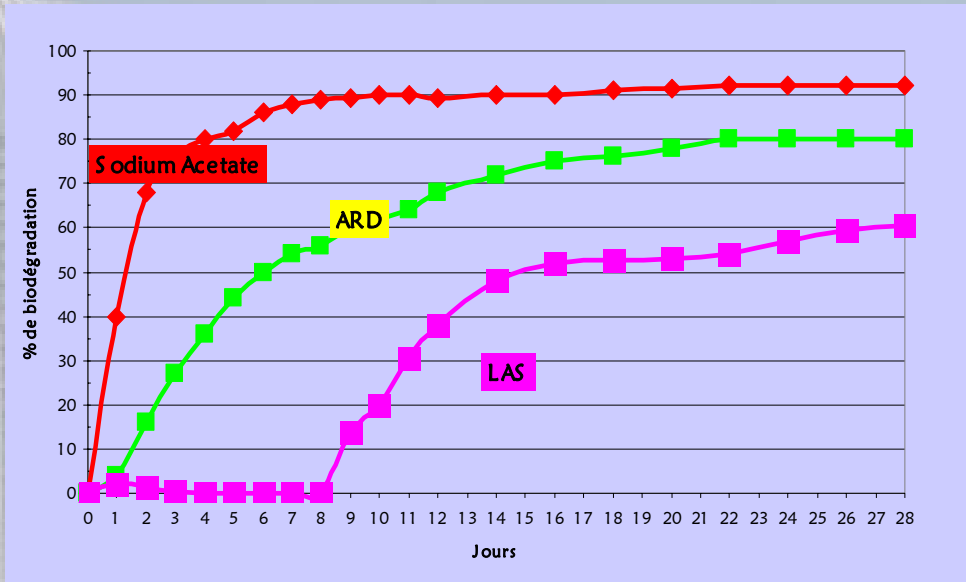
Perfumes	Solubilizers tested					
	A.R.D.	Cremophor RH 40	Transcutol	ORAMIX BG14	AG 6206	Tween 20
Lemon (Huber the Nose 19-11454)	5,8 - 7,2	4,3	> 28,7	> 15,0	> 17,2	nd
Pine OSF France 34230	5,0	5,0	> 26,0	> 13,7	> 13,8	5,0
Grapefruit OSF France	4,1	5,3	> 26,6	> 12,0	> 12,0	4,0
Mint OSF France 20636	2,6	5,1	> 25,5	> 9,5	> 9,5	2,6
Peach OSF France 20668	5,1	7,6	> 25,0	9,5	9,5	5,0

Solubilizer / perfume (g / g) until complete solubilization in water

Efficiency with essential oils, cosmetic ingredients (α-bisabolol…)

Environmental considerations

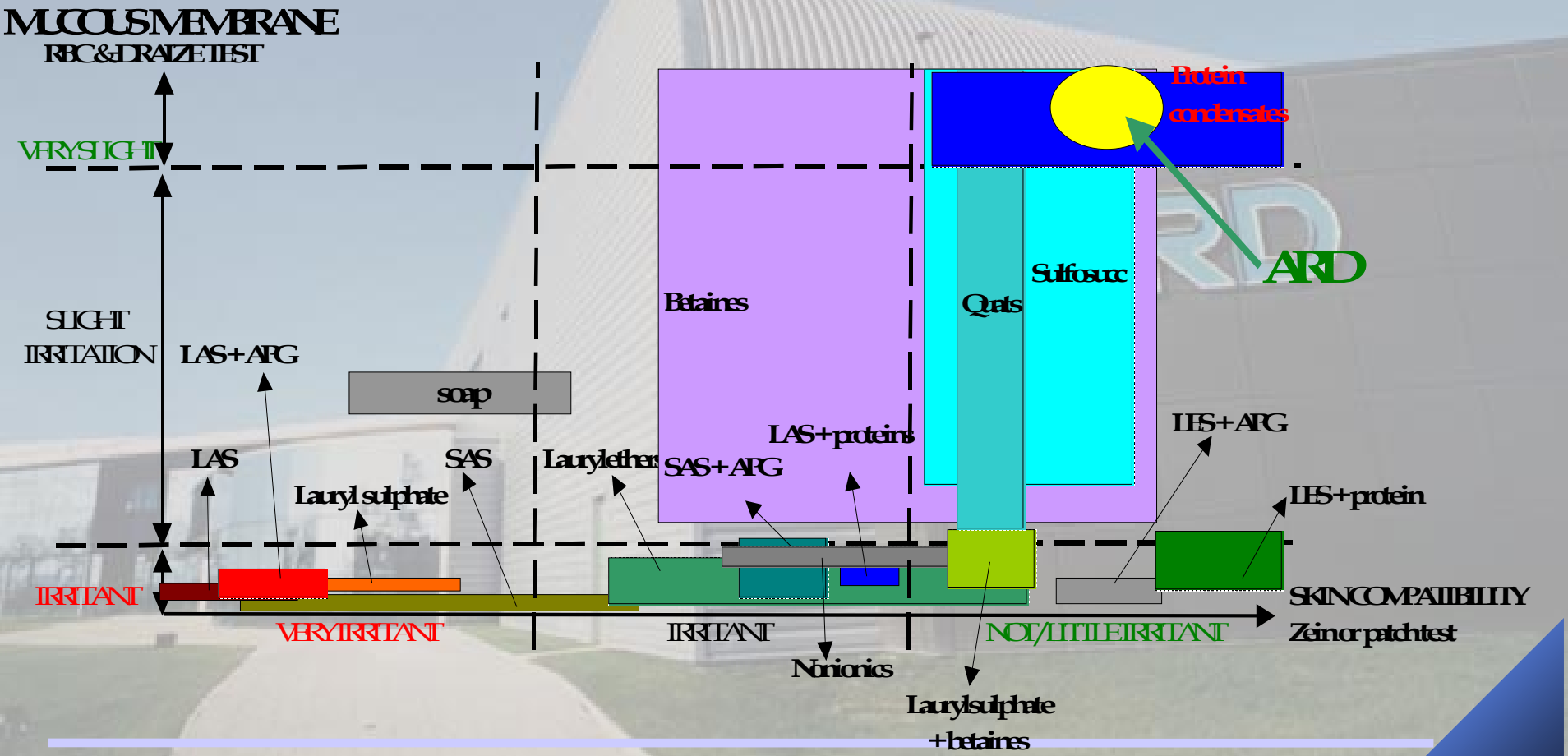
- **Ultimate biodegradability along EOCD 301F**



- **Favorable eco-toxicity**

Environmental considerations

- Smooth surfactants



CONCLUSIONS

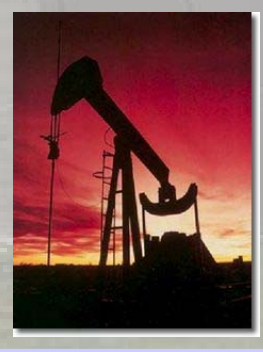
1. Renewable raw materials for low cost surfactants
2. Co-products from the patented process could be valorised
3. Low energy consumption process (<90°C with pentoses to >110°C with Glu)
4. High biodegradability according to OECD 301F, equal to sodium acetate
5. Not irritant product (RBC and Zein test), especially for skin
6. Broad range of applications

PRODUCTION OF NEW SURFACTANTS FROM CEREAL CO-PRODUCTS BY GREEN CHEMISTRY

A·R·D

AGRO INDUSTRIE RECHERCHES ET DEVELOPPEMENTS

Wheat APP



SOLIANCE

Thank you for attention