Sustainable Materials in Fast Moving Consumer Goods Formulations

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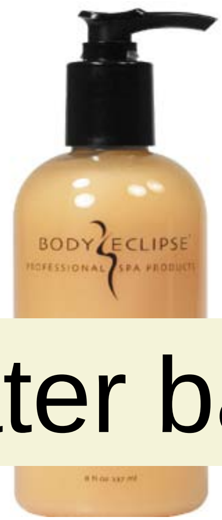
Black and Green? Birmingham 14 April 2010

JLS ChemConsult Ltd

Context

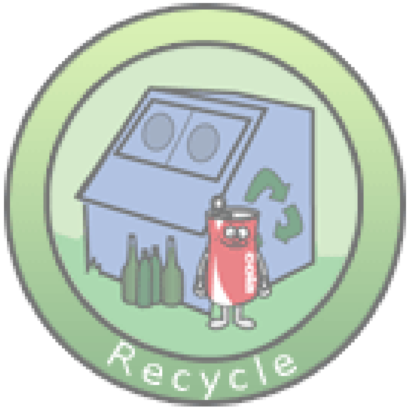
- Personal care products



Water based formulations

Context

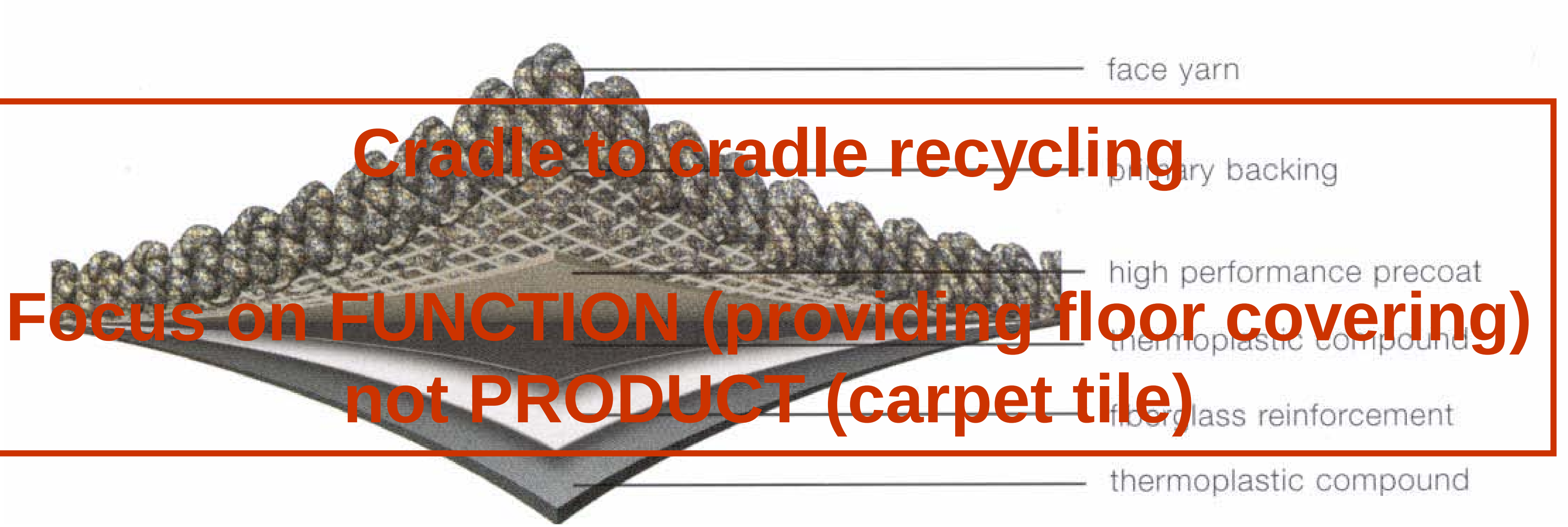
- Reduce, reuse, recycle?



Function *vs.* product

Ecoworx carpet tiles

“100% recyclable. Completely PVC-free. EcoWorx offers three high-performance cradle to cradle backings to meet your every need. Each is backed with a lifetime commercial warranty and an **environmental guarantee** for reclamation and recycling.”

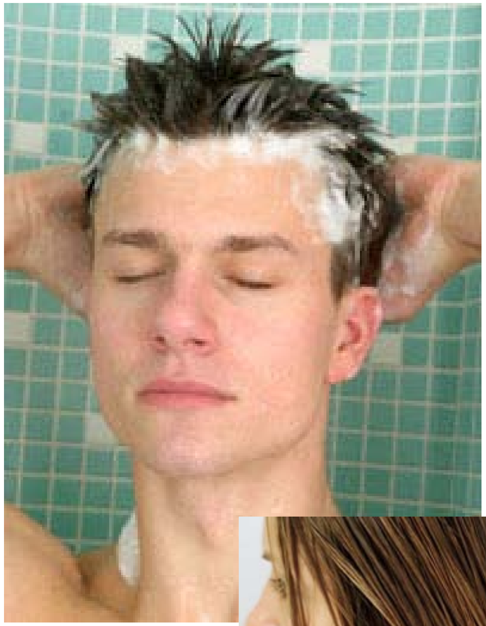


Cradle to cradle recycling

Focus on FUNCTION (providing floor covering) not PRODUCT (carpet tile)

http://www.shawcontractgroup.com/Html/EnvironmentalEcoworx

Function



cleaning

Viscosity / Rheology

- Suspension
- Flow
- Dispensing
- Usability
- Feel

Structuring water

thickening

Surfactants and structuring

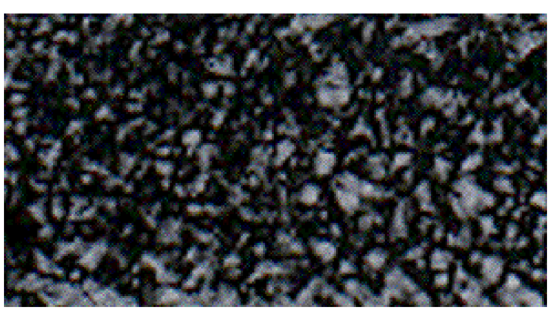
Abundant, cheap material
From renewable resources
100 % non-petrochemical
Not food competitive
Clean derivatisation
Biodegradable
Functional
Gentle

structuring
foaming
cleaning

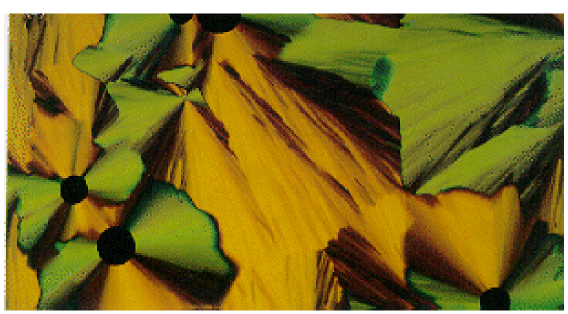
Environmental & commercial sustainability

Thickening strategies

- Natural polymers
  e.g. gums, starch,
  carrageenans
- Synthetic polymers
  e.g. PEGs, acrylate co-polymers
- Surfactant mesophases



hexagonal



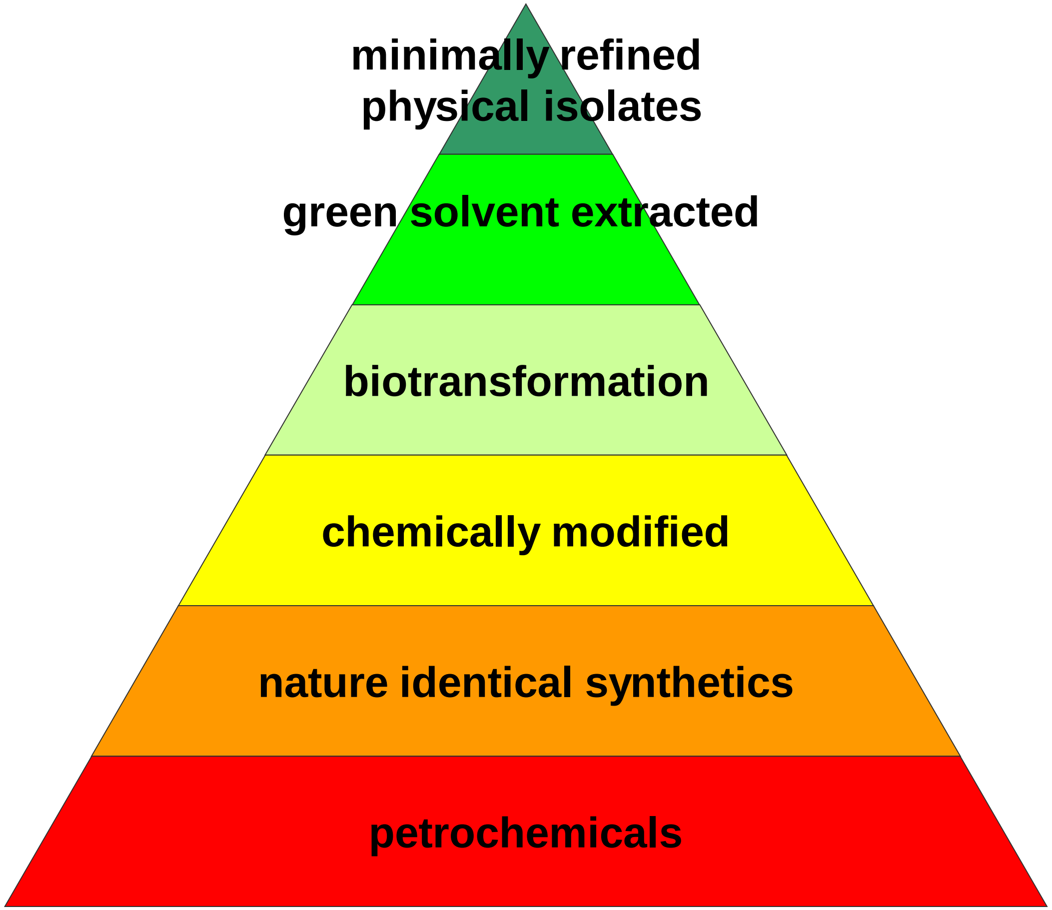
lamellar

Retain function / reduce resource use

Opportunity to save resources;
Cost saving to pay for new ingredient;
Other opportunities?

The growing “natural” market

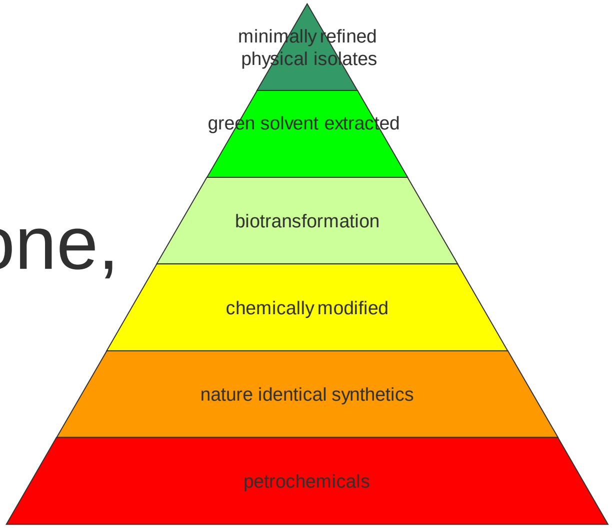
Changing context; shift to bio-source



Question for the formulator

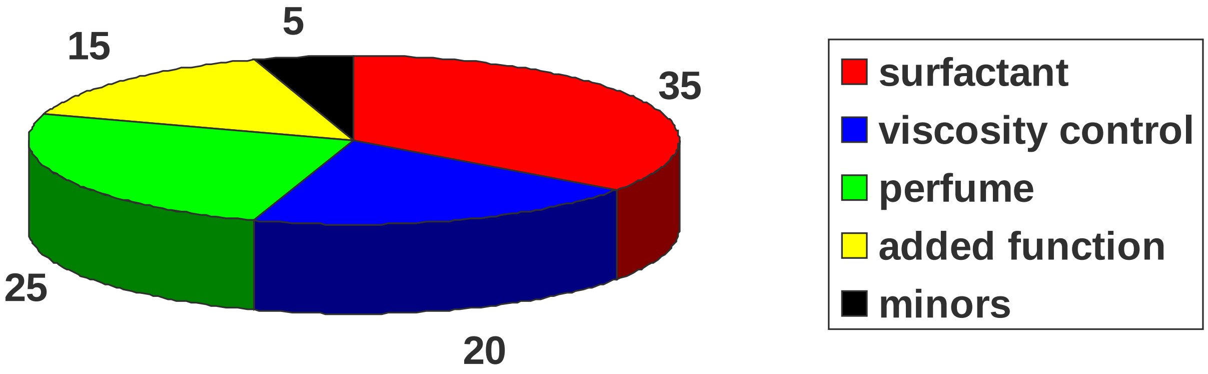
- "natural", "nature derived", "renewable" etc. do not equate with "less impact on environment"
- Need to consider scale, energy intensity, competing land requirements etc.
- Do we get the best result by taking existing approaches and substituting individual components?

If you do what you've always done, you'll get what you always got.



Formulation vs. Components

- Substituting individual components is difficult; they have been optimised w.r.t. cost and function
- Function is not as neatly compartmentalised as the diagram suggests; “formulator’s art”!
- Need to look at cost and function of formulation, not individual components
- Environmental performance / sustainability is also a function of formulation



Cellulose – an abundant biopolymer

700 000 000 000 *t* = total volume

40 000 000 000 *t* = renewed annually

100 000 000 *t* = feedstock usage p.a.

4 000 000 *t* = dissolving pulp for high $ applications

Cellulose

- Abundant
- Not food competitive
- “Waste” sources
- Renewable
- Non-petrochemical

Background

Sustainability Research in the Development of Fast Moving Consumer Goods (SUSRES)

MARIE CURIE ACTIONS
Marie Curie Host Fellowships,Transfer of Knowledge (ToK)
Development Host Scheme
MTKD-CT-2005-029644

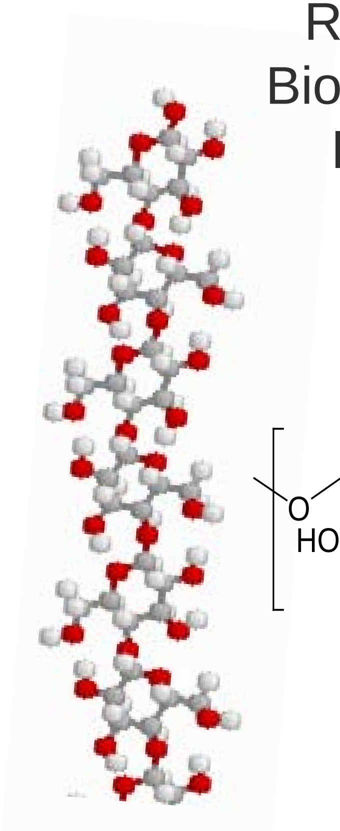
Functional, Renewable & Sustainable Hybrid (FR&SH) materials

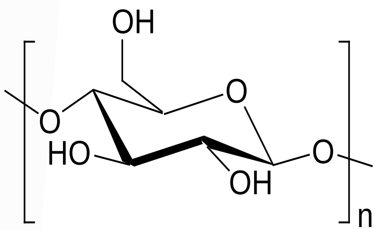
TSB "Sustainable Materials" collaborative R&D project

A cellulose based structurant?

Underivatised cellulose

Abundant
Renewable
Biodegradable
Insoluble



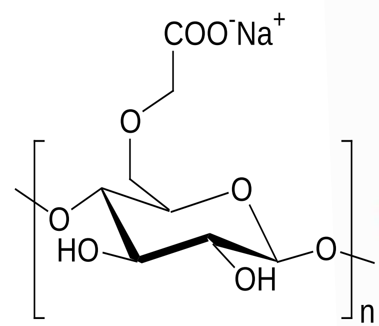


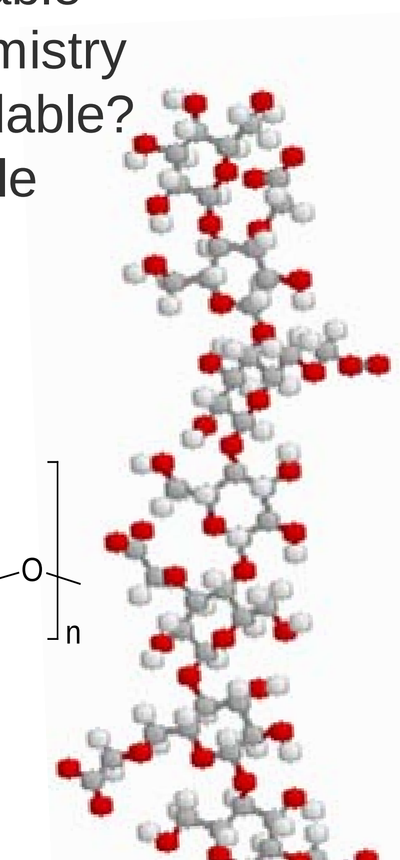
??

A material that retains some of the cellulose structure, but is maleable;
Retain H-bonding, but rendered “soluble”;
Minimal processing;
Minimal chemical transformation.

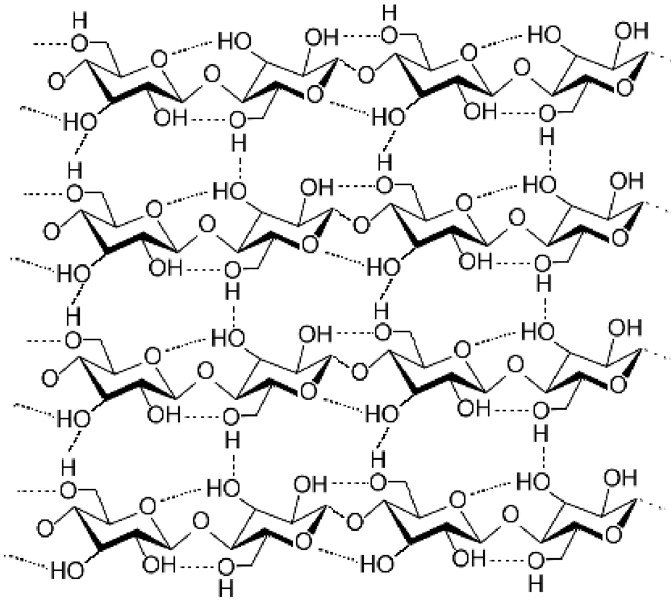
Cellulose derivatives

Renewable
Dirty chemistry
Biodegradable?
Soluble



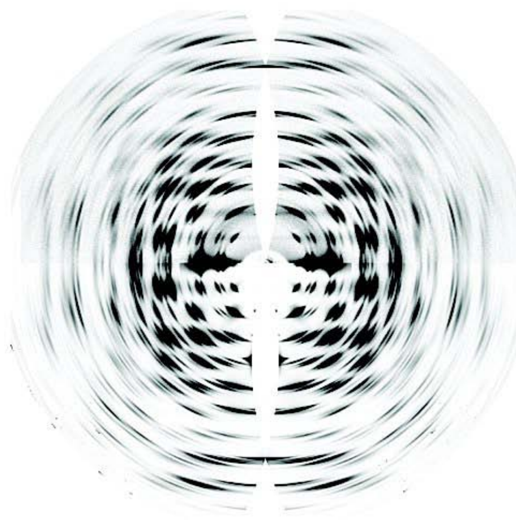


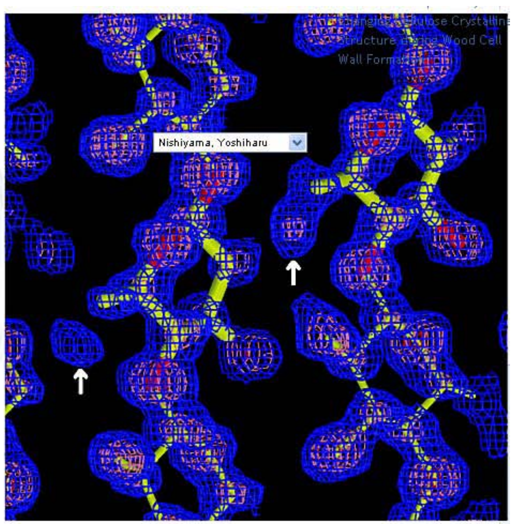
Cellulose is insoluble



Tends to form hydrogen bonds

May have crystalline regions





Dispersed fibrils of oxidised cellulose

Underivatised cellulose

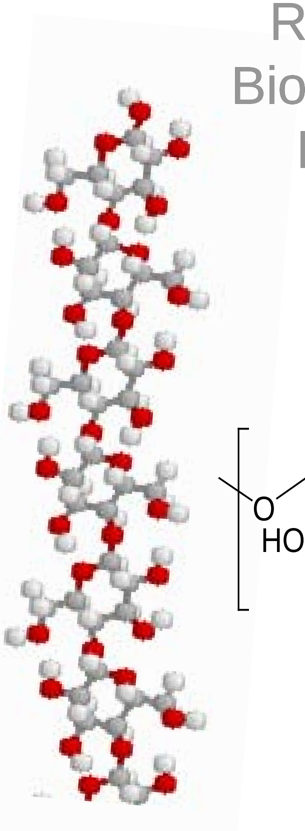
Abundant
Renewable
Biodegradable
Insoluble

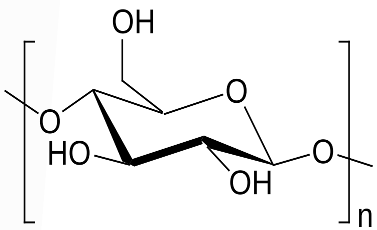
Dispersed oxidised cellulose

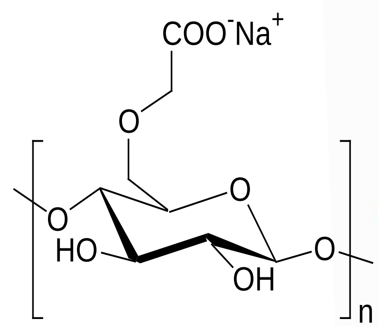
Renewable
Clean chemistry
Biodegradable
Dispersible

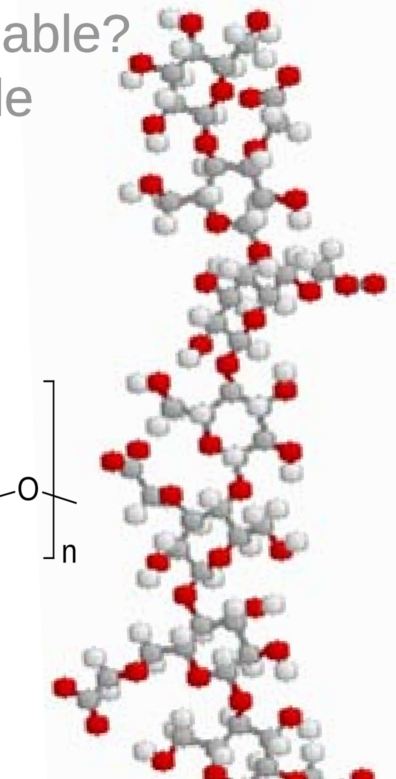
Cellulose derivatives

Renewable
Dirty chemistry
Biodegradable?
Soluble



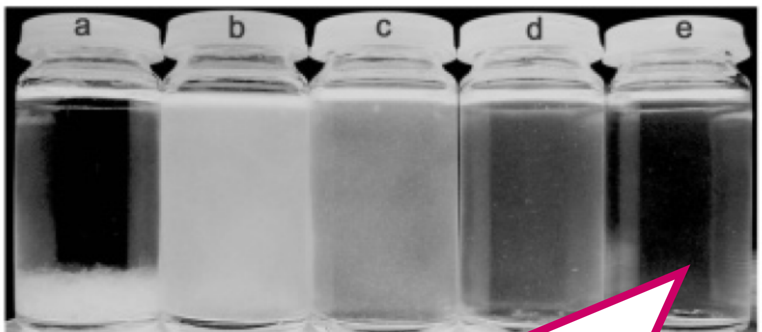






Precedent

- Fully C(6) oxidised cellulose = glucuronic acid; soluble but tends to be unstable
- Partially C(6) oxidised, dispersed cellulose[1]



Stable, viscous, slightly turbid dispersion - shear thinning.[1]

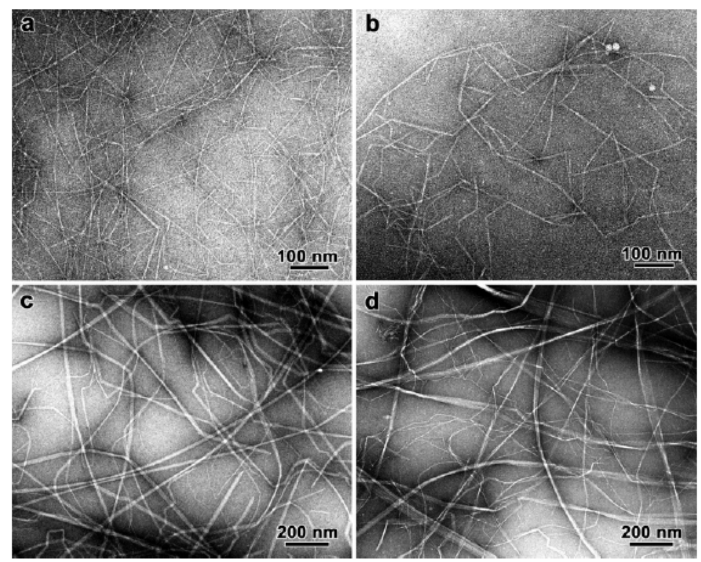


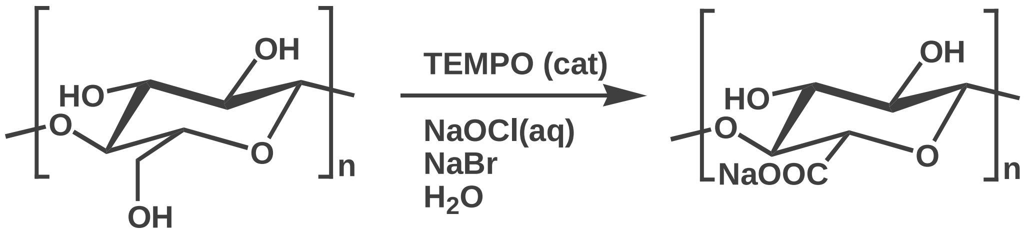
Figure 4. Transmission electron micrographs of cellulose microfibrils disintegrated after TEMPO-mediated oxidation of never-dried samples: (a) bleached sulfite wood pulp, (b) cotton, (c) tunicin, and (d) bacterial cellulose. The preparations were negatively stained with uranyl acetate.

1. Saito *et al*., *Biomacromol*., 2006, **7**, 1687.

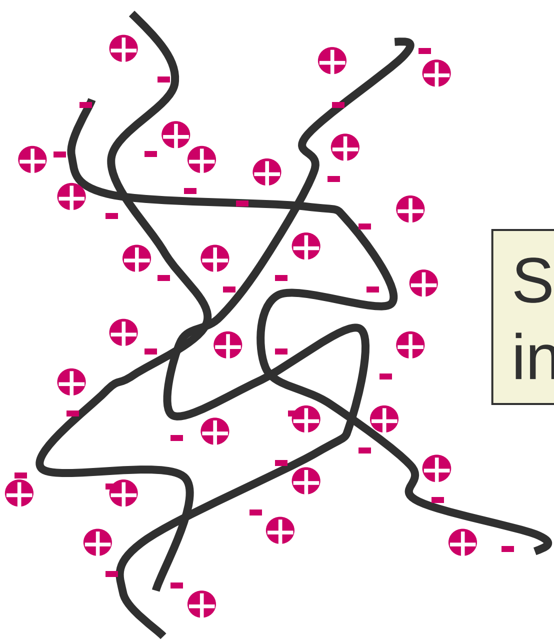
C6 Oxidised cellulose; a KNOWN product

- Hemostat
- Degraded/absorbed
- Bacteriostatic
- Long shelf life
- Used >100M times

Clean processing



“lightly” oxidised cellulose fibrils, dispersed by sonication, yield thick translucent solutions at low wght %



Surfactant interactions?

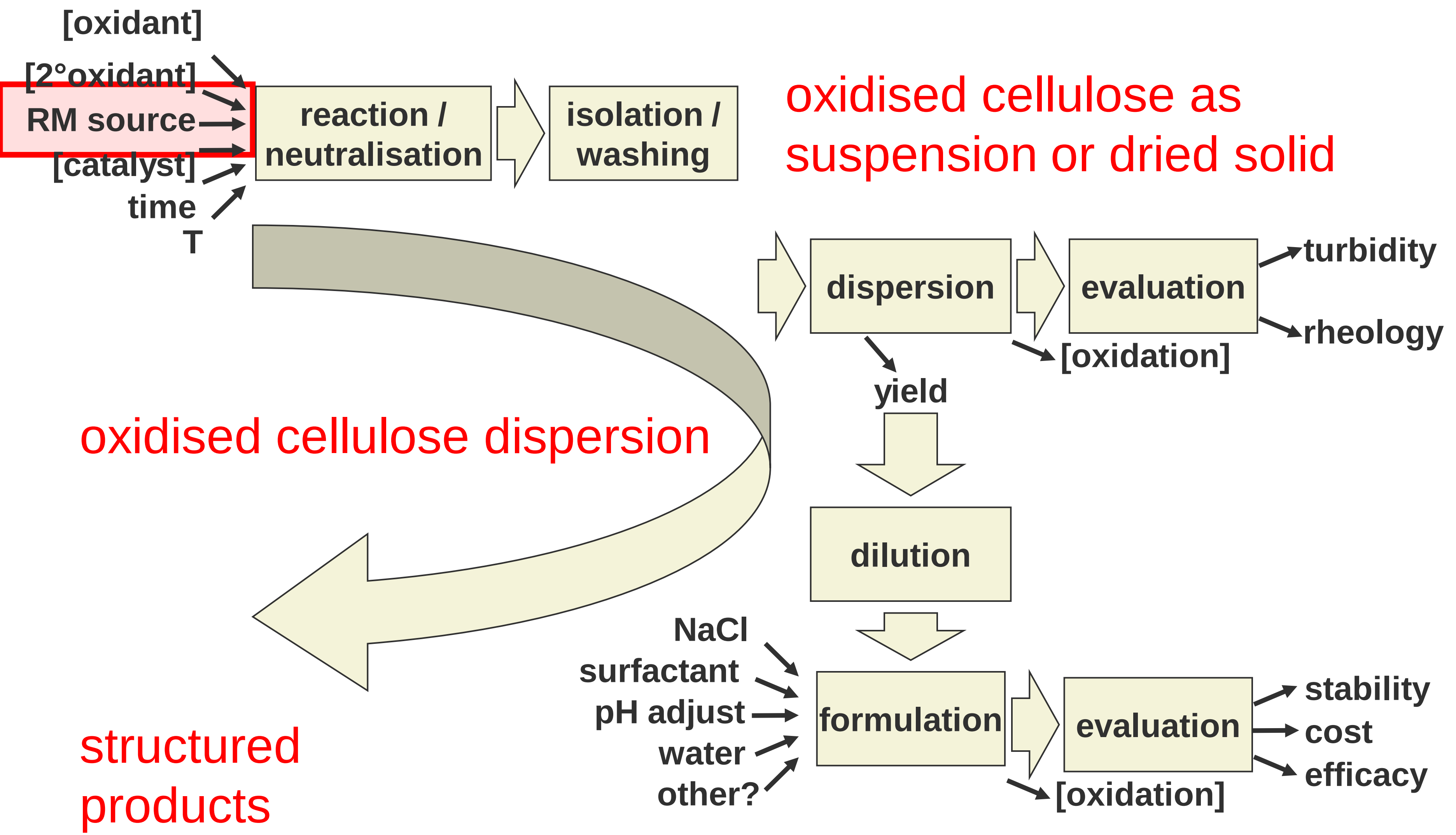
Thixotropic gels

Not dissolved, but well-dispersed fibrils with surface charge; bacterial cellulose X SCMC hybrid

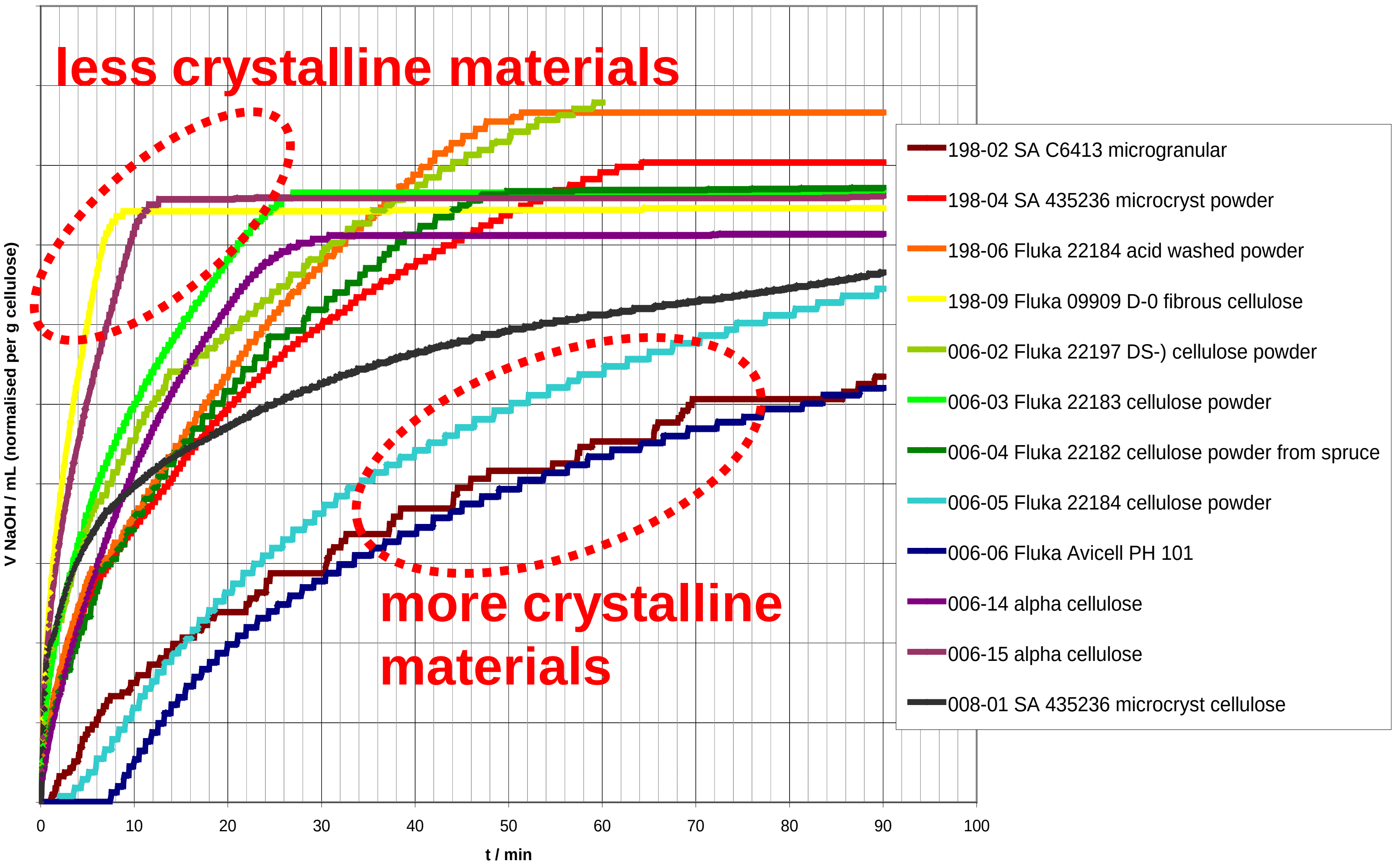
Sample personal care formulations

- ~5 % surfactant, ~1 % oxidised cellulose dispersion in water
- Shear thinning, stable gel
- Smooth texture, pleasant feel
- Readily dispersed in water

Processes


[oxidant]
[2°oxidant]
RM source
[catalyst]
time
T
reaction / neutralisation
isolation / washing
oxidised cellulose as suspension or dried solid
dispersion
evaluation
turbidity
rheology
[oxidation]
yield
oxidised cellulose dispersion
dilution
NaCl
surfactant
pH adjust
water
other?
formulation
evaluation
stability
cost
efficacy
[oxidation]
structured products

Comparison of cellulose sources

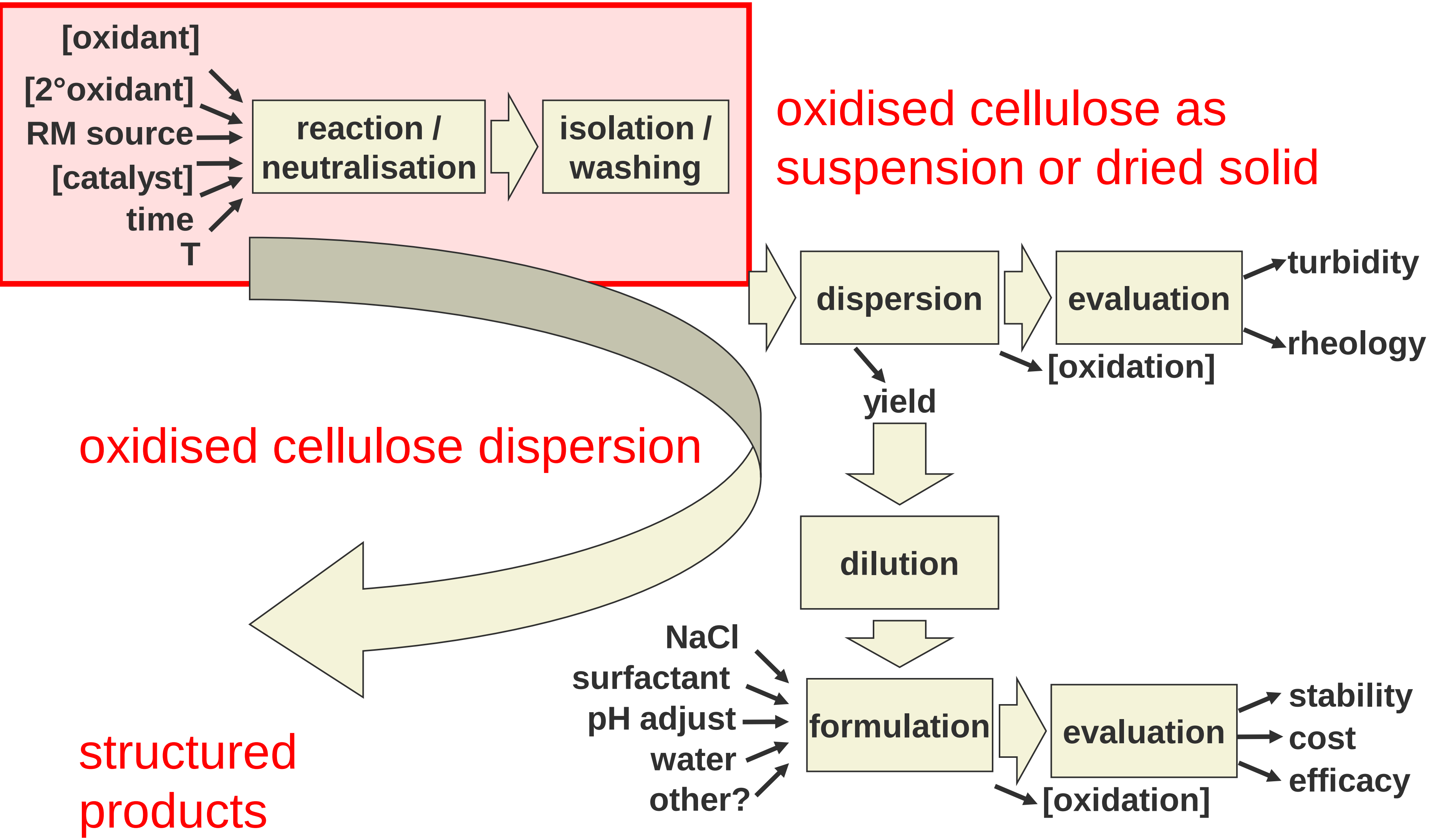


Corrected for LOD of cellulose; normalised; const ratio cellulose:catalyst:oxidant

Raw materials

- Least processed provides most rapid oxidation
- Contains greatest α-cellulose content and smallest crystalline fraction
- A bleaching process!

Processes


[oxidant]
[2°oxidant]
RM source
[catalyst]
time
T
reaction / neutralisation
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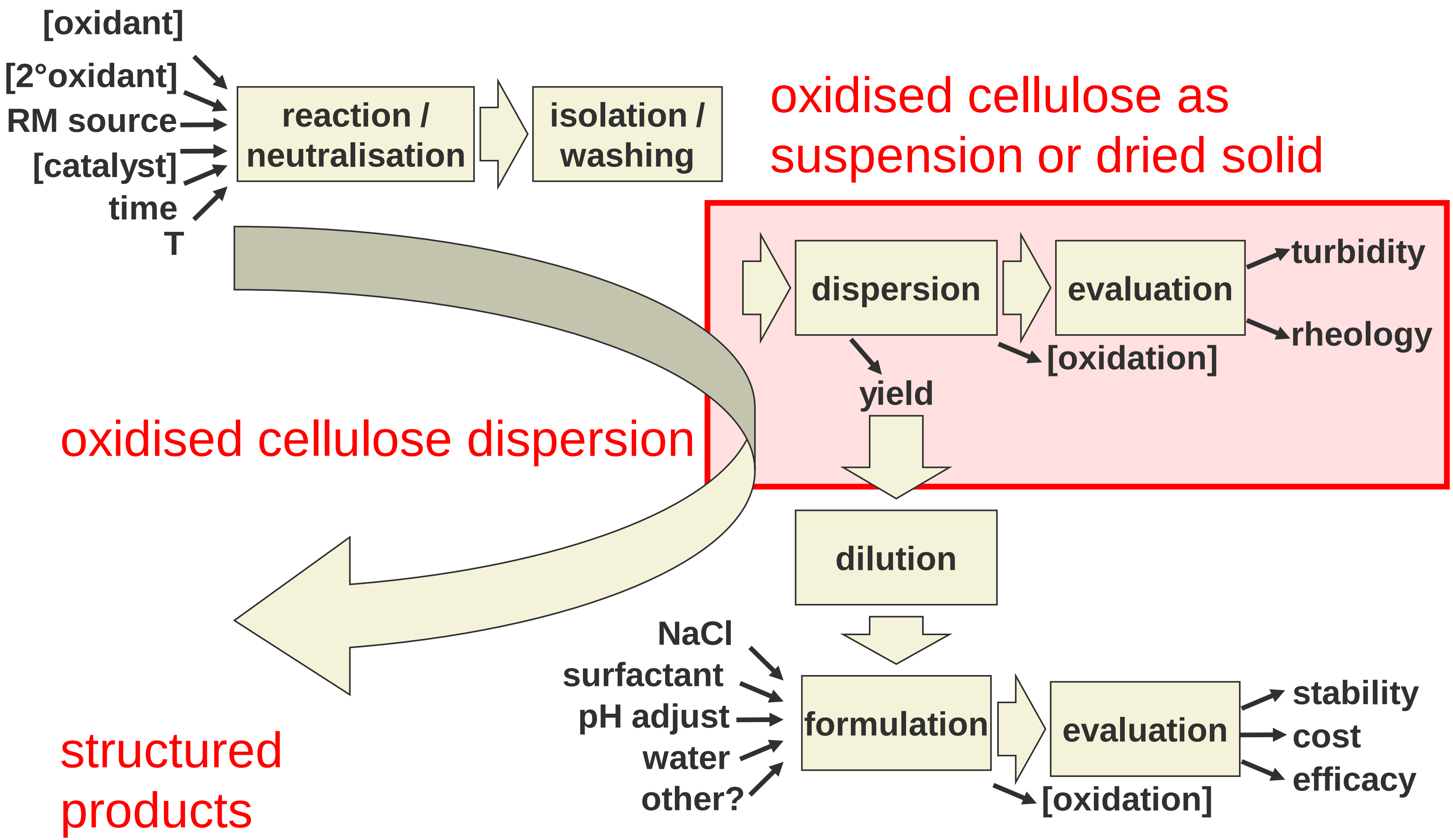
oxidised cellulose as suspension or dried solid
dispersion
evaluation
turbidity
rheology
[oxidation]
yield
oxidised cellulose dispersion
dilution
NaCl
surfactant
pH adjust
water
other?
formulation
evaluation
stability
cost
efficacy
[oxidation]
structured products

Mapping reaction requirements

- Titrino modified as multi-reaction station; pH control and tracking
- Variation of reagent, catalyst concentrations, T, etc.
- Direct comparison of reaction rate & extent
- Degree of oxidation
- Record pH / neutralisation quantities in reports

Processes


[oxidant]
[2°oxidant]
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evaluation
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yield
oxidised cellulose dispersion
dilution
NaCl
surfactant
pH adjust
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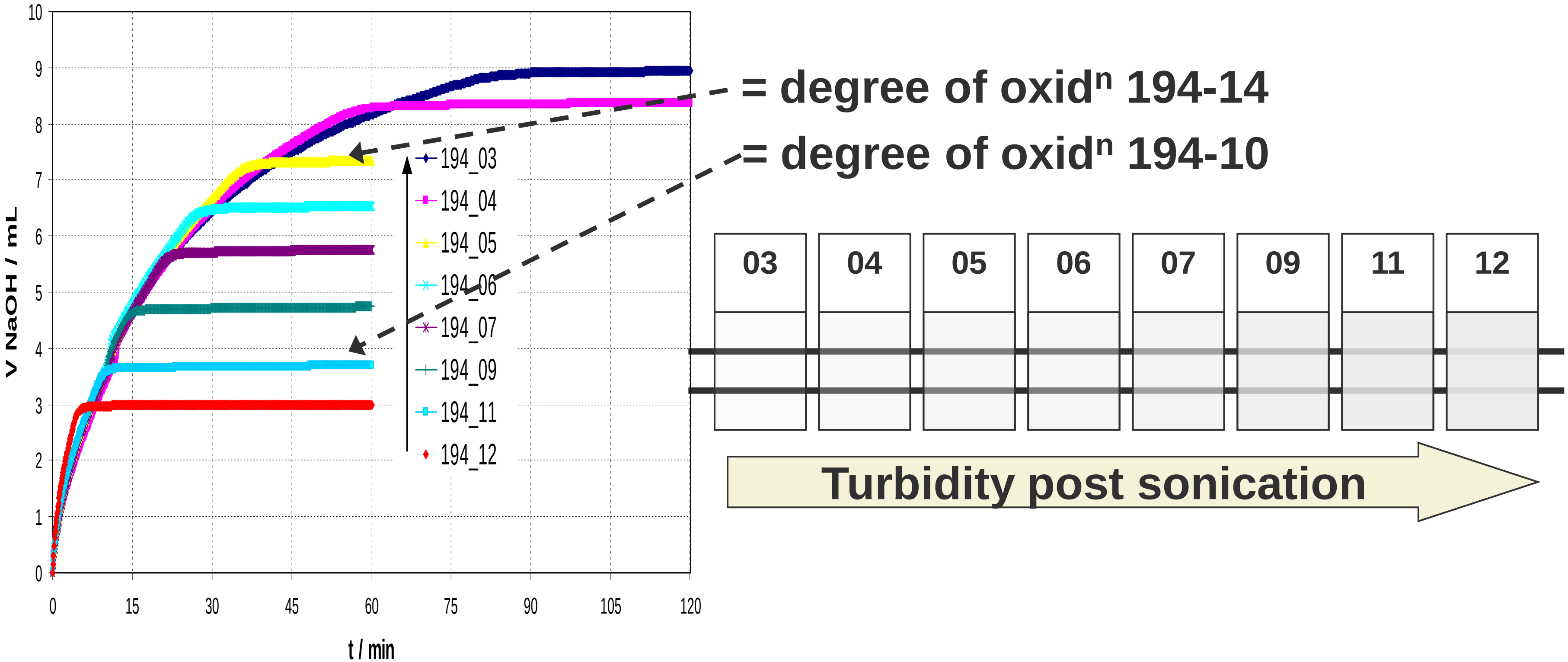
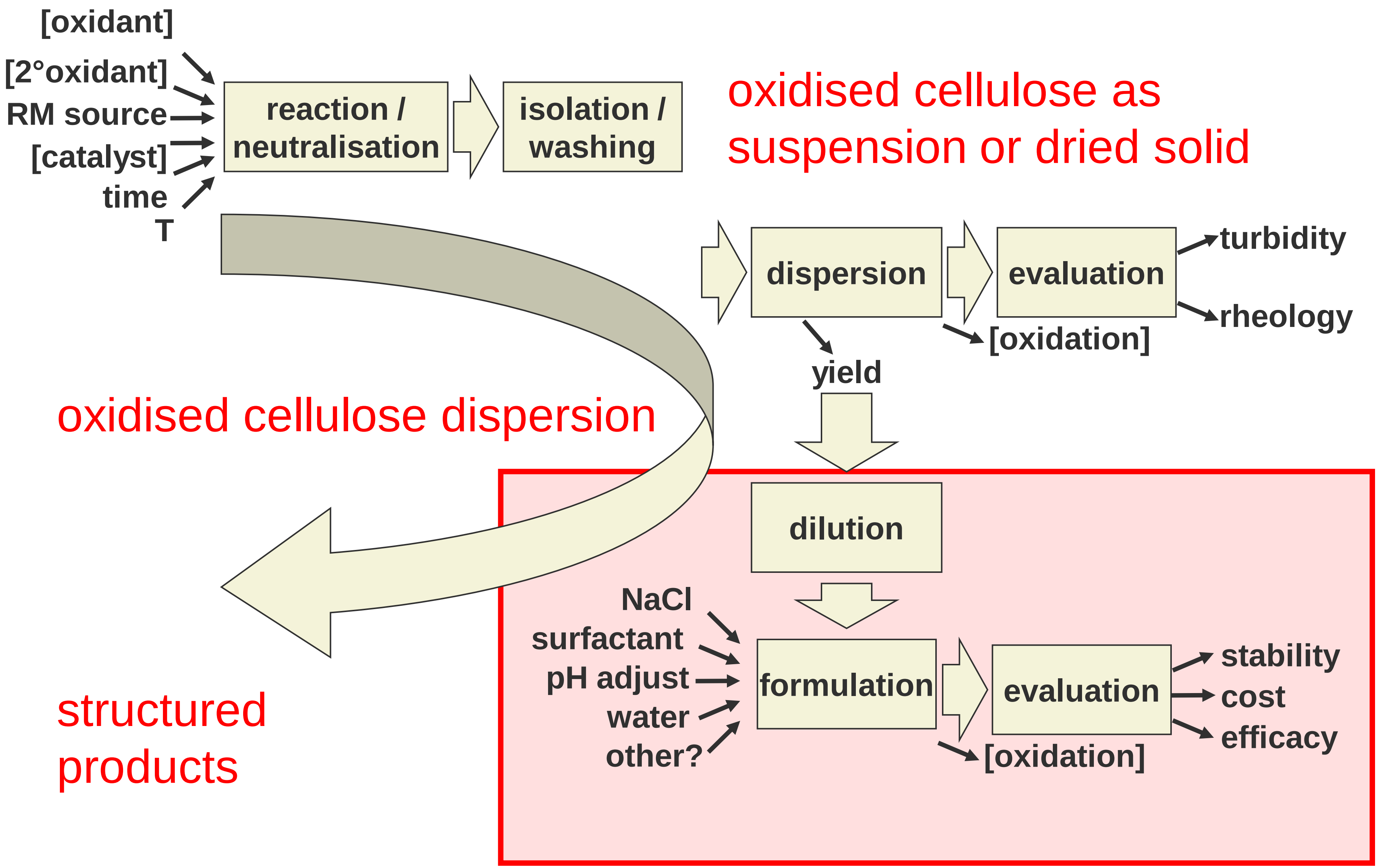
other?
formulation
evaluation
stability
cost
efficacy
[oxidation]
structured products

Extent of oxidation



- 194-14 approx twice as oxidised as 194-10
- 194-14 quite turbid post sonication – sonicate for extra 10 min @ 30 % power to clear
- Add solid salts and dissolve

Processes


[oxidant]
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formulation
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cost
efficacy
[oxidation]
structured products

Formulation considerations

- Surfactant type / charge?
- Effect of pH?
- Other formulation ingredients?
- Salt concentration?
- Other ions/salts?

  E.g. Ca^{2+} cross-linked gels from polyglucuronic acid (soluble oxidised cellulose) are known

surfactants

anionic ☑ zwitterionic ☑ nonionic ☒

Dispersed, oxidised cellulose; SLES 1EO (as used in shampoo formulations); NaCl; pH adjusted to 6 (w HCl$_{(aq)}$)

		1	2	3	4	5	6	7	8	9	10	11	12				
no surfactant (control)	**ox cell / %**	0.5	1.0	1.5	0.5	1.0	1.5	0.5	1.0	1.5	0.5	1.0	1.5				
	NaCl / %	0.0	0.0	0.0	0.2	0.2	0.2	1.0	1.0	1.0	2.0	2.0	2.0				
	Surf / %†	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0				
		Free flowing – water-like	Free flowing – water-like	Free flowing	Free flowing some solid? (little)	Free flowing some solid? (little)	Free flowing – some thickening	Free flowing – some thickening	Single mass medium/soft gel	Firm mass of gel – shows syneresis	Single mass – soft gel (some liquid?)	Single mass medium gel	Gelled mass of particles				
					13	14	15	16	17	18	19	20	21				
no NaCl	**ox cell / %**	See 1	See 2	See 3	0.5	1.0	1.5	0.5	1.0	1.5	0.5	1.0	1.5				
	NaCl / %				0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0				
	Surf / %†				2.5	2.5	2.5	5.0	5.0	5.0	10.0	10.0	10.0				
					Free-flowing liquid	Free-flowing liquid – smbll qubnt gel sep	Free-flowing liquid some thickening	Free flowing liquid	Gelled mass – soft - flows	Gelled mass – firm – exhibits syneresis	Single mass soft gel*	Gel particles tending to form mass	Concs not accessible				
							22	30 (23 rep)	33 (24 rep)		34 (25 rep)	31 (26 rep)	35 (27 rep)		36 (28 rep)	32 (29 rep)	37 (30 rep)
surf and NaCl / 1 ox cell conc	**ox cell / %**	See 2	See 5	See 8	See 11	See 14	1.0	1.0	1.0	See 17	1.0	1.0	1.0	See 20	1.0	1.0	1.0
	NaCl / %						0.2	1.0	2.0		0.2	1.0	2.0		0.2	1.0	2.0
	Surf / %†						2.5	2.5	2.5		5.0	5.0	5.0		10.0	10.0	10.0
							Single mass soft gel	Gel particles tending to form mass – free flowing	Gel particles tending to form mass – free flowing		Gel particles – tending to form mass – free flowing	Gel particles form mass – float when aerated	Gel particles – free flowing		Ge particles form mass – float when aerated	Gel particles – free flowing	Gel mass – pours slowly

* breaks up on shaking; † SLES 1 EO supplied as 70 % active % calculated taking this into account

Dispersed, oxidised cellulose; SLES 3EO (as used in concentrated laundry); NaCl pH adjusted to 8 (w $HC1_{(aq)}$)

no surfactant (control)						1			2			3					
	ox cell / % **NaCl / %** **Surf / %†**	0.5 0.0 0.0	1.0 0.0 0.0	1.5 0.0 0.0	0.5 0.2 0.0	1.0 0.2 0.0	1.5 0.2 0.0	0.5 1.0 0.0	1.0 1.0 0.0	1.5 1.0 0.0	0.5 2.0 0.0	1.0 2.0 0.0	1.5 2.0 0.0				
						Discarded – error in delivery V			Single mass medium/soft gel			Single mass medium gel – tends to particles					
no NaCl						4			5			6					
	ox cell / % **NaCl / %** **Surf / %†**	0.5 0.0 0.0	1.0 0.0 0.0	1.5 0.0 0.0	0.5 0.0 2.5	1.0 0.0 2.5	1.5 0.0 2.5	0.5 0.0 5.0	1.0 0.0 5.0	1.5 0.0 5.0	0.5 0.0 10.0	1.0 0.0 10.0	1.5 0.0 10.0				
						Free-flowing liq – v. slightly thickened			Gel particles tend to form mass**			Gel particles tend to form firm mass**					
surf and NaCl / 1 ox cell conc							7	8	9		10	11	12		13	14	15
	ox cell / % **NaCl / %** **Surf / %†**	1.0 0.0 0.0	See 1	See 2	See 11	1.0 0.0 0.0	1.0 0.2 2.5	1.0 1.0 2.5	1.0 2.0 2.5	See 4	1.0 0.2 5.0	1.0 1.0 5.0	1.0 2.0 5.0	See 5	1.0 0.2 10.0	1.0 1.0 10.0	1.0 2.0 10.0
							Single mass soft gel – flows on shaking	Single mass medium/firm gel	Gel particles – free-flowing		Gel particles tending to form single mass**	Gel particles form mass but break up easily	Gel particles free-flowing but thick		Gel particles tending to form mass	Gel particles tending to form mass (trap air bubbles)	Concs not accessible

* breaks up on shaking; ** convert to free-flowing with gel particles on shaking; ; † SLES 3 EO supplied as 70 % active - % calculated taking this into account

Mechanism of gelation / thickening?

- NaCl OR surfactant yield gels
- Effect appears to be additive (qualitative)
- Gels known with bridging ions e.g. Ca^{2+}
- Effect of chaotropes / kosmotropes?

chaotropes	**kosmotropes**
large, charge diffuse ions	small, charge dense ions
interfere with stabilizing intra-molecular interactions	stabilise/structure water-water interactions

- Test NaCl, NaBr, KI, $CaCl_2$, urea (non-ionic, chaotrope)

Effect of added chao/kosmotropes

Oxidised cellulose (more oxidised); 1.5 % dispersion in H_2O					
Salt/addit.	none	NaCl	NaBr	KI	$CaCl_2$
Mass %	-	1.1	2.1	3.5	1.5
Mol %	-	0.020	0.020	0.021	0.013
	Free-flowing	Slightly thickened	Slightly thickened	Slightly thickened	Ppt gel particles

Oxidised cellulose (less oxidised); 1.6 % dispersion in H_2O					
Salt/addit.	urea	NaCl	NaBr	KI	$CaCl_2$
Mass %	0.9	0.8	1.6	2.3	0.1
Mol %	0.015	0.015	0.015	0.014	0.001
	Free-flowing	gel	gel	gel	Free-flowing

no effect - nonionic chaotrope

some Ca^{2+} tolerance

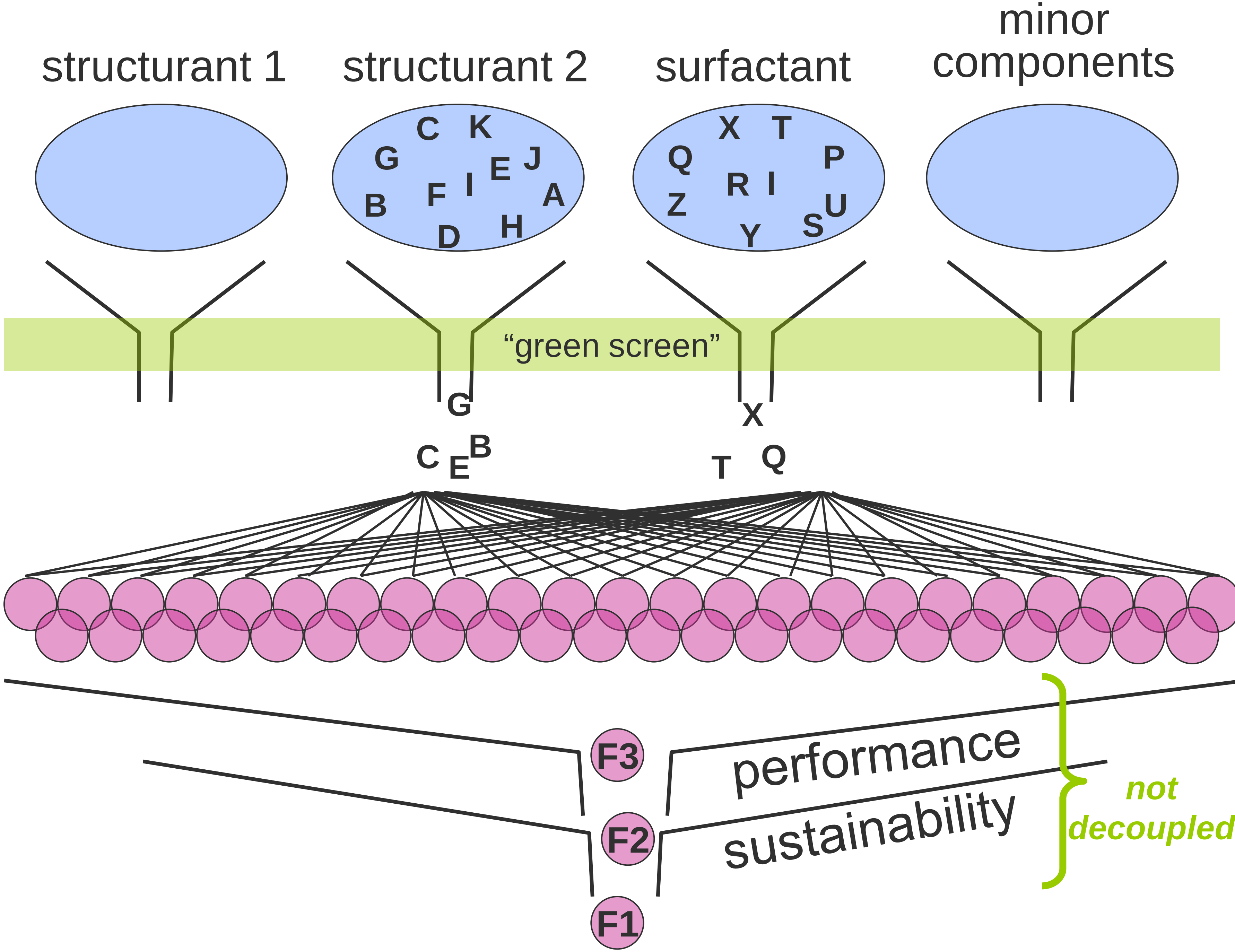
Benefits

Green Chemistry	Renewable resource?	Green process?*	Non-hazardous product?
Raw material	Cost effective raw material?	Raw material availability? Non-petrochem?	Not food competitive?
Product	Formulation compatibility?	Product performance?	Customer benefit?
End of life	Reduced surfactant (and other) content?	Biodegradable?	Reduced environmental burden?

* A.E. de Nooy, A.C. Besemer, H. van Bekkum, J.A.P.P. van Dijk, J.A.M. Smit, *Macromolecules*, 1996, **29**, 6541-6547 and numerous later publications from van Bekkum's group

Characteristics of sample formulations

- Suspension of finely divided solids / bubbles
- Stable for many months
- Odourless
- Colourless/white
- Required:
  - Challenge testing (no bugs grown in many months)
  - closer definition of regions of thickening – HT exps with ranges of solids/surfactants/salt
  - Structurant specifications: degree of oxidation; RM source (cellulose type) etc.



structurant 1
structurant 2
surfactant
minor components
C K G E J B F I A D H
X T Q P R I Z U S Y
"green screen"
G
C E B
X
T Q
F3
F2
F1
performance
sustainability
not decoupled

Sustainability metrics in reformulation

- For individual components:
  - What to measure?
  - Scarce data availability for R&D materials
  - Comparison of disparate materials from different sources & prepared by different routes

The Green Screen for Safer Chemicals defines four benchmarks on the path to safer chemicals:

- Benchmark 1:
  Avoid—Chemical of high concern
- Benchmark 2:
  Use but search for safer substitutes
- Benchmark 3:
  Use but still opportunity for improvement
- Benchmark 4:
  Prefer—Safer chemical

Sustainability metrics in reformulation

- For individual components:
  - What to measure?
  - Scarce data availability for R&D materials
  - Comparison of disparate materials from different sources & prepared by different routes

… but a major difficulty is that comparison of individual materials or ingredients does not work for <u>complete reformulation</u> with new ingredients, i.e. <u>not</u> one for one replacement of ingredients.

Formulated product *vs* ingredients

If formulated product should be compared - how to compare formulations that contain completely different ingredients?

Possible methodologies?

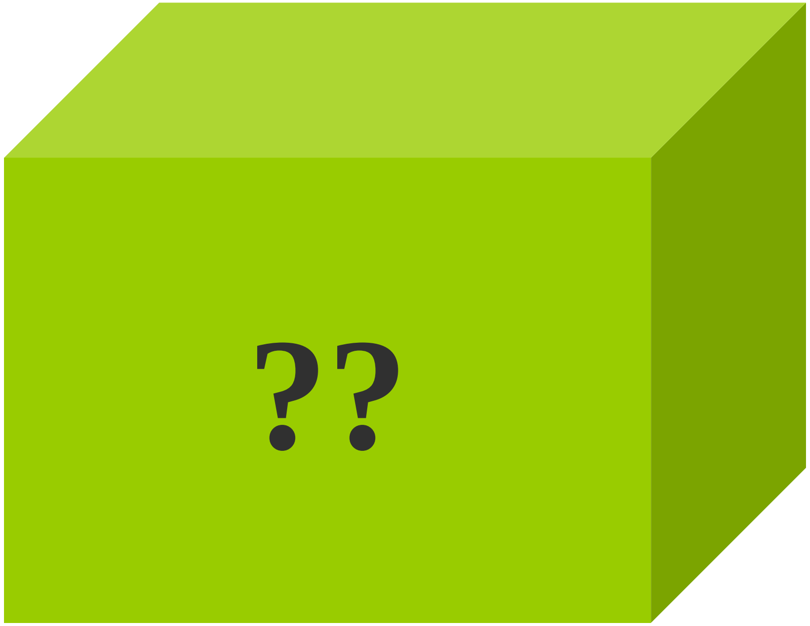
- Life Cycle Assessment (LCA):
  - Environmental aspects ONLY
  - Appropriate for final product, too detailed for early development / selection
  - “Unit of Service” concept may be useful
- Software based LCA type analyses
  - e.g. CCaLC
- Streamlined Life Cycle Assesment (SLCA)
  - Developed by Forum for the Future and Natural Step
  - A big picture approach

[redacted]

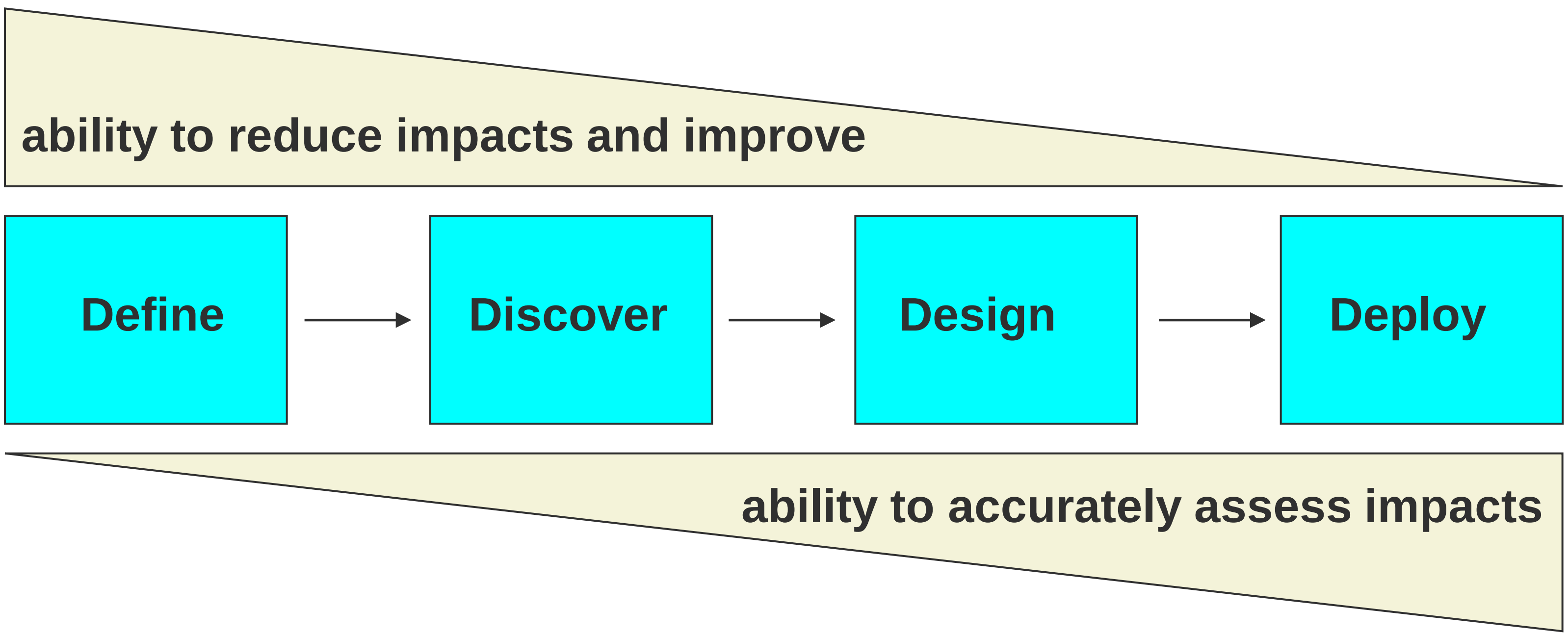
First Layer Questions		System Conditions			
		Virgin Materials from Earth's Crust	Persistant Materials	Degradation of Nature	Working Conditions
Life Cycle Stages	Raw Materials				
	Manufacture				
	Packaging & Distribution				
	Use				
	End of Life				

Key					
	Good	Quite Good	Weak	Bad	Don't Know
Answers	All positive	Mostly positive	Mostly negative	All negative	
System Condition	Met	Partly met	Mostly not met	Not met	Can't judge

Does this work for what is **inside** the box?



If “80-90% of environmental impacts are determined at the early design stages” … (DEFRA/UK Design Council)



… need to start to use environmental impact as a differentiator in early discovery

Cost "per unit structuring"; *f*(function)

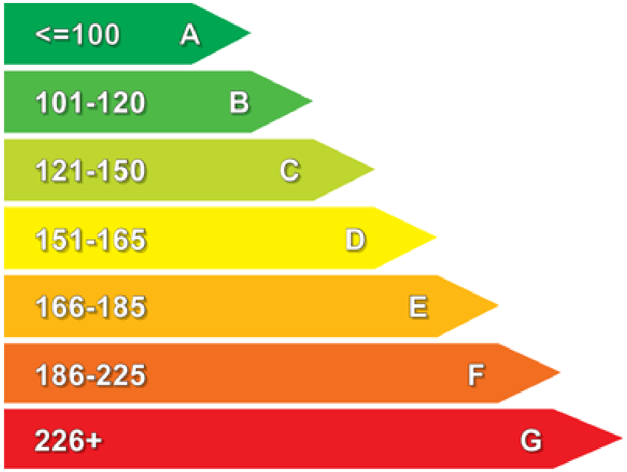
- The like for like comparison may be *function* based
- Bang for buck!
- Cost per unit funct... concept can be ...ded to environm... ...ost

No greenwash

Credibility, credibility, credibility

e.g. CO_2 produced per unit structuring

- CO_2 bandings / CO_2 footprint are becoming familiar



- Numerical
- Allows comparison of disparate structurants … or even different structuring mechanisms
- Data is available for a range of ingredients: surfactants, structuring polymers etc.

Summary

- Dispersed oxidised cellulose

Wide application

- Flow characteristics are important in many products for diverse applications


051-06
051-07

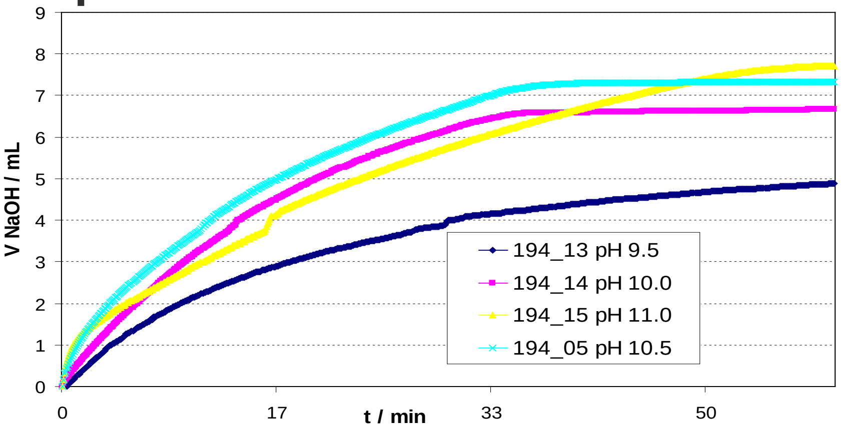
- Concluding comments

Questions:

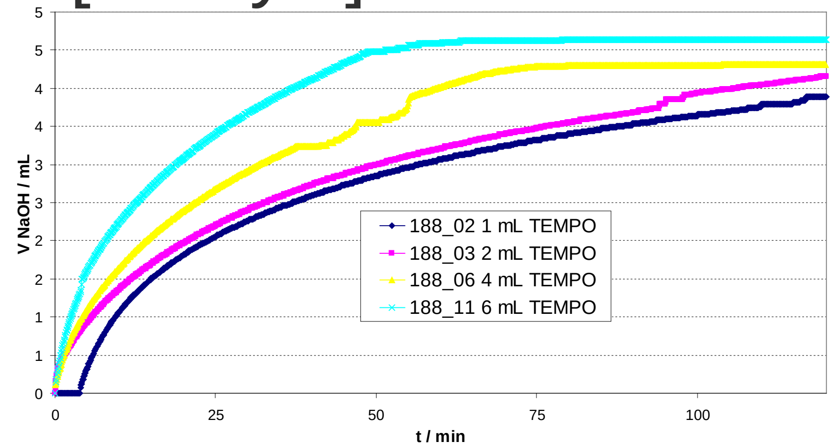
1. What are the specific purposes of sustainability reporting?
2. Who will the outcomes be reported to?
   (Are there different audiences?)
3. What are the boundaries?
   (Are these different for the different audiences?)
4. What functional unit will form the basis for sustainability reporting and comparison?
5. Which ingredients or classes of ingredients will be considered?
6. Who are the key suppliers and contacts?

Reaction conditions, T = 25 °C

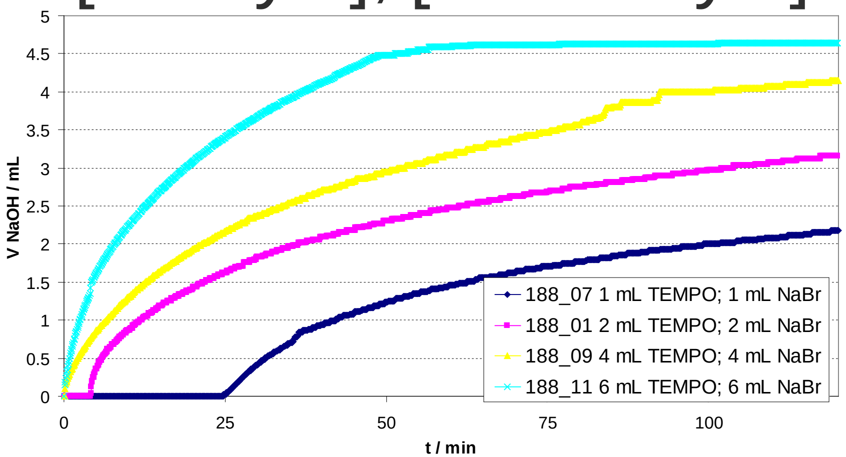
pH



[catalyst]



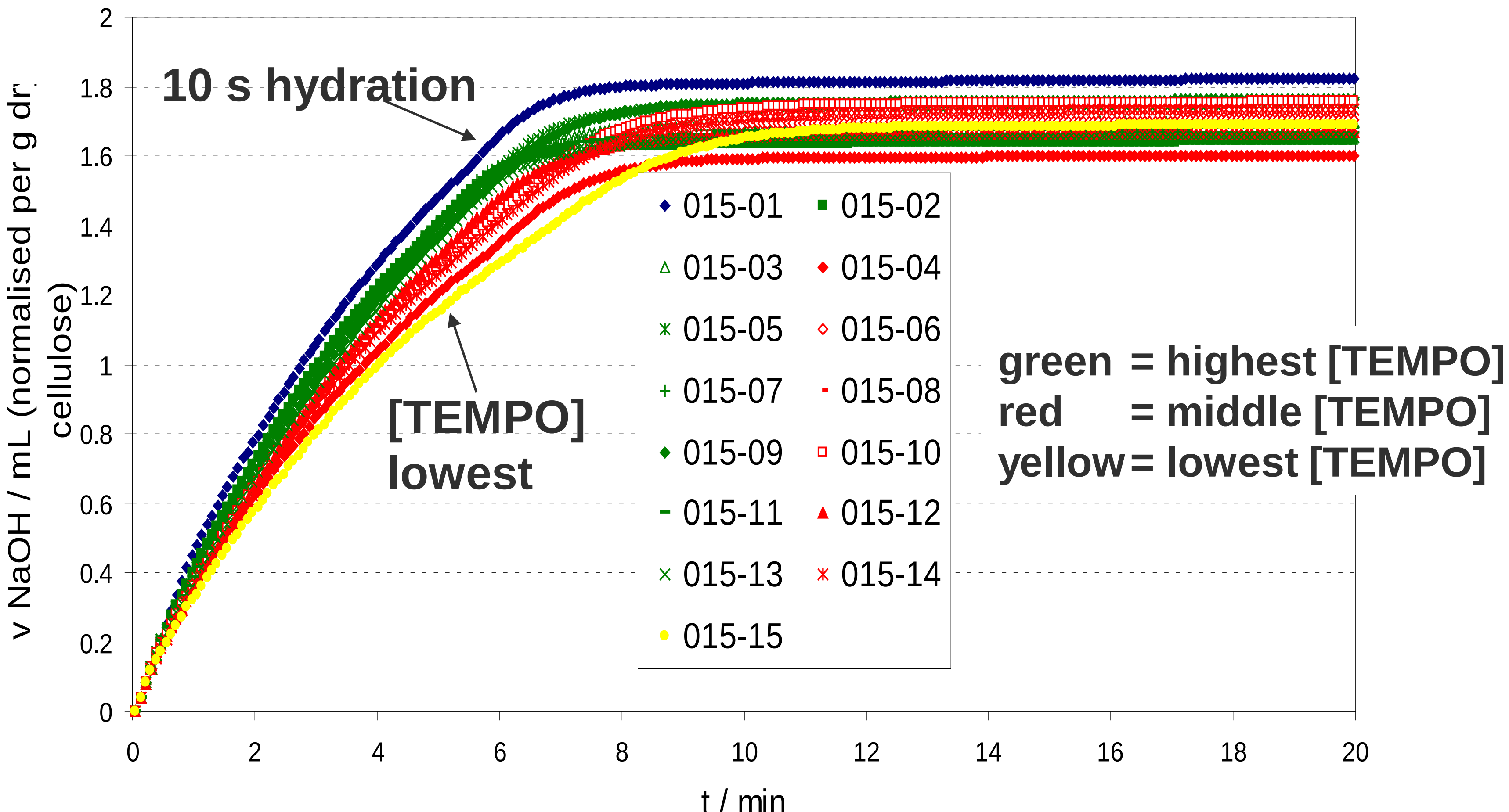
[catalyst], [co-catalyst]



- Optimum pH = 10.5 (10-11)
- Reducing [TEMPO] & [NaBr] slows rate of conversion more significantly than [TEMPO] alone
- [TEMPO] can be minimised

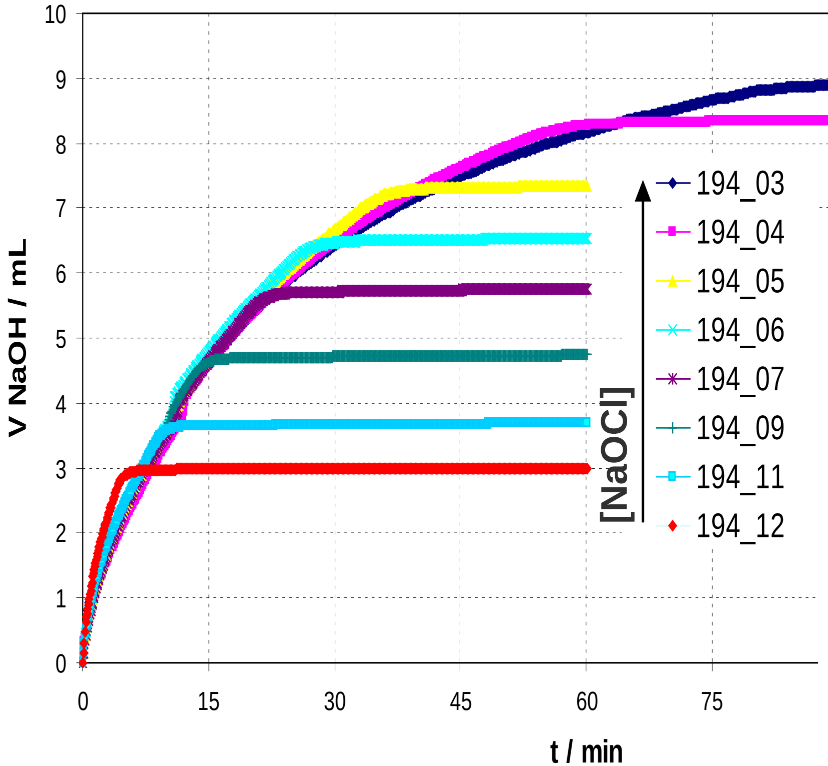
Reproducibility

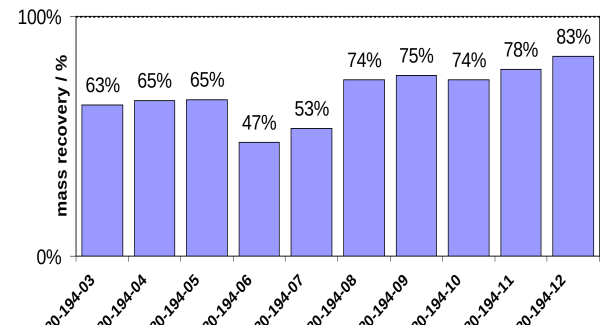
- Const [NaBr], [NaOCl], pH, T, 300 s hydration time

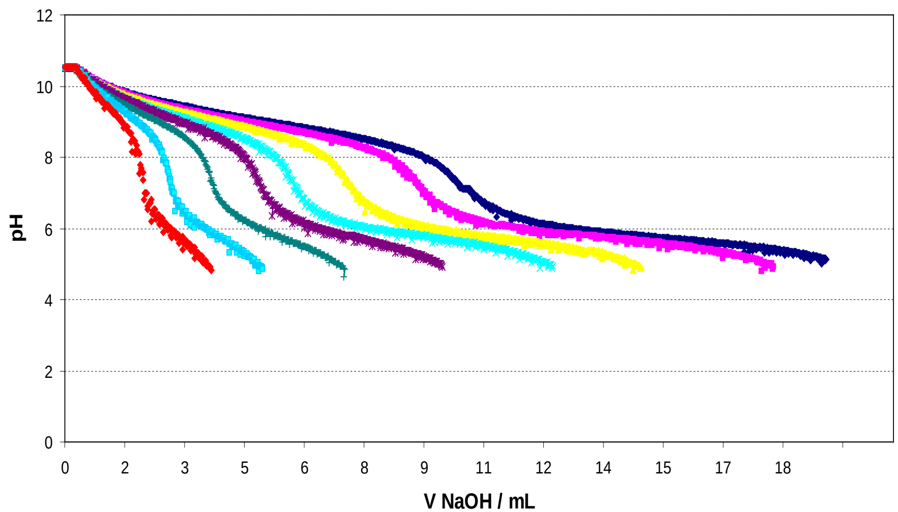


Mapping degree of oxidation

- Readily followed by NaOH consumption
  (possib. sources of error include: acid groups on cellulose; other species oxidised; consumption of oxidant by degradation mechanisms not associated with substrate ox.)







Quantify turbidity of dispersions and compare in single “formulation”