Biorefinery, the bridge between agriculture and chemistry

Greening Agriculture and Nitrogen

Copenhagen, 24 April 2013

Johan Sanders, professor Biobased Commodity Chemicals

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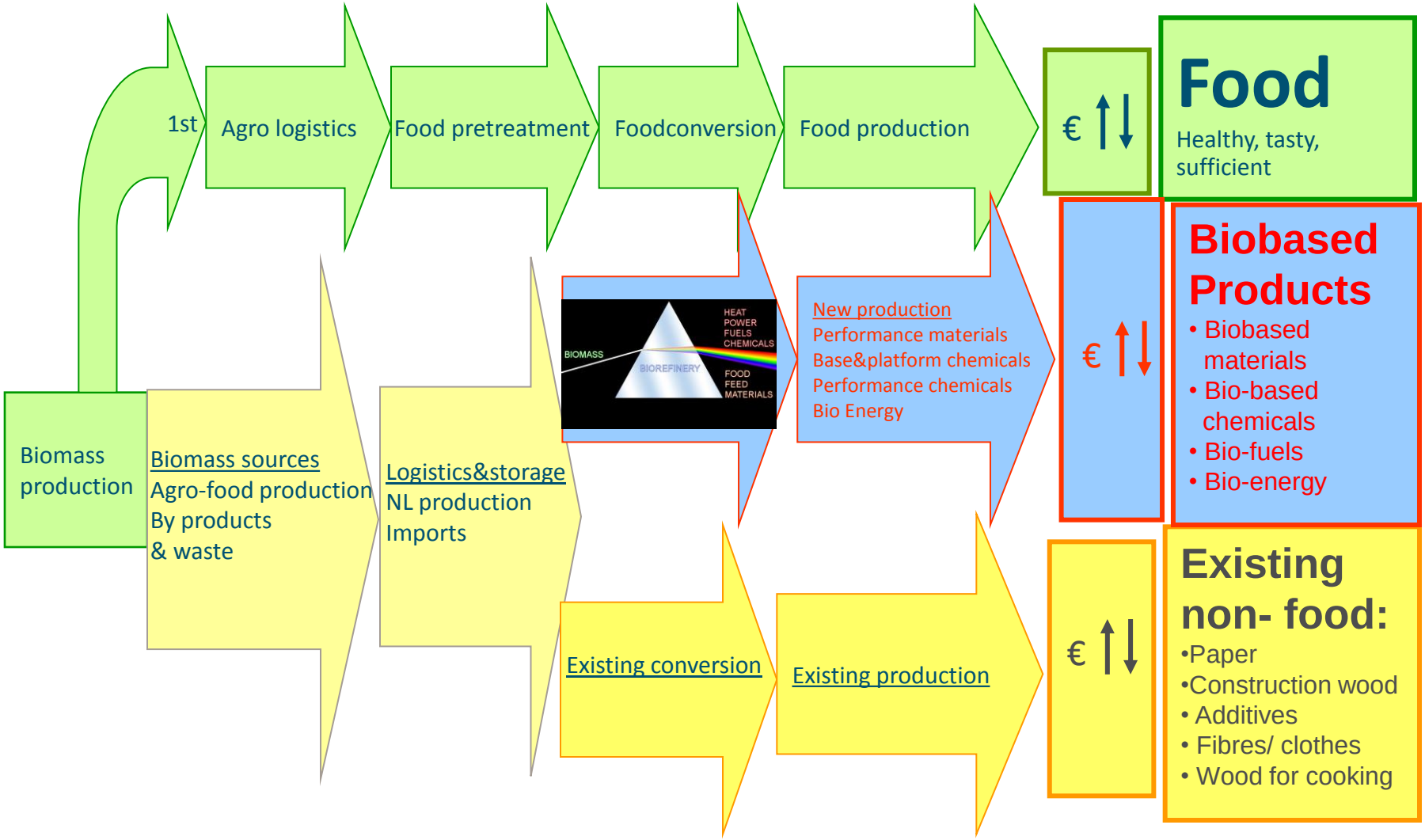
The new challenges in a biobased Economy:



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Biomass use today and in 2050

	Mton
▪ Food incl. feed*	4 – 5000
▪ Wood, paper, cotton	2000
▪ Wood for cooking	4000
▪ 30% of 1000EJ in 2050=	20 000
▪ All bulkchemicals in 2050	600(= 2000 input!)

* Excluding grass and seafood

Design rules for a sustainable Bio-economy

- Increase field yield but *keep components on the field that are required for soil fertility*
- Use all biomass components and *choose the right raw material*
- Use each component at its highest value:

  (molecular) structure is much better than caloric
- Reduce capital cost to speed up innovation and *to benefit from small scale without the disadvantages*

How do these design rules work out for N?

- Annually 140 M tonnes of NH3 is produced worldwide
- Appr 120 Mtonnes is used as fertilizer, 10 Mtonnes as chemical feedstock
- Agriculture produces about 600M tonnes of protein (including natural protein production this is appr 3000M tonnes)
- Human population requires about 70-100M tonnes of protein
- Dependent on feeding regimes cattle get appr 4-5 times more protein than ends up in milk and meat, for pigs this is appr. 3 times. And actually is misused
- A lot of the surplus 500 M tonnes of protein is 'misused' as fertilizer (eg beet leaf), as feedstock for biogas(eg corn), for power generation (wheat grids), used at a too low value (most residues in animal feed), 30% of food is not consumed!
- Cattle and pigs and poultry can get much more tailored protein/ amino acids without increasing the costs
- ***Higher efficiency leads to lower NH3, N2O, NO3 emissions***

F - ladder

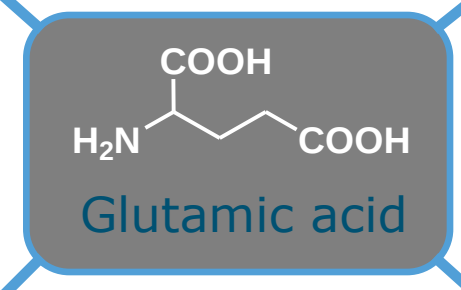
How to get the best value from biomass?

	€/ton
Farma	High
Fun	High
Food ingredients	5 - 20000
Food nutritional	100-500
Feed young	100-500
Feed pigs	100-300
Feed cattle	50-250
Functional chemical	500-800
Fibre	500
Fermentation	150-400
Fermentation bulk	100-300
Fuel	100-300
Fertilizer	-/- 200-100
Fire	50-150
Flare	0
Fill	-/- 300

Use of plant molecular structures

N-Vinylpyrrolidone

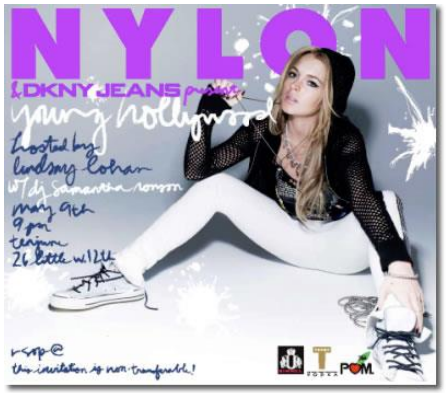
Acrylonitrile



Glutamic acid

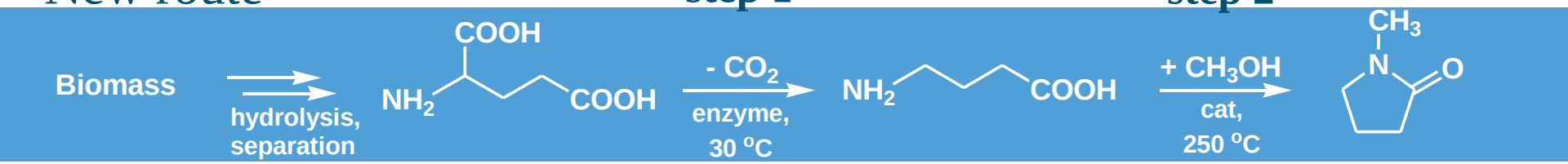
N-Methylpyrrolidone

Diaminobutane

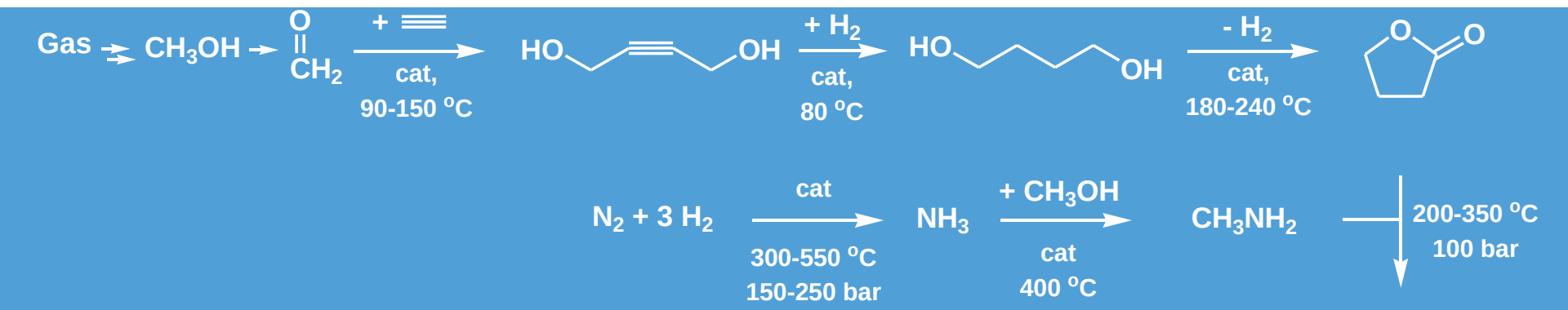


The route to NMP, new vs conventional

New route



Conventional route



Amino acids contain N and O.

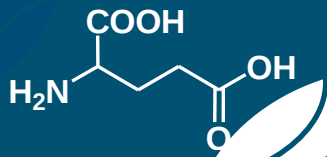
Less steps (= factories) & energy for the same product!

Biobased NMP, makes an ethanol plant profitable

500 Million liters bioethanol

(~ 400 kton) =200M€

360 kton DDGS (~130 € / ton) =46M€

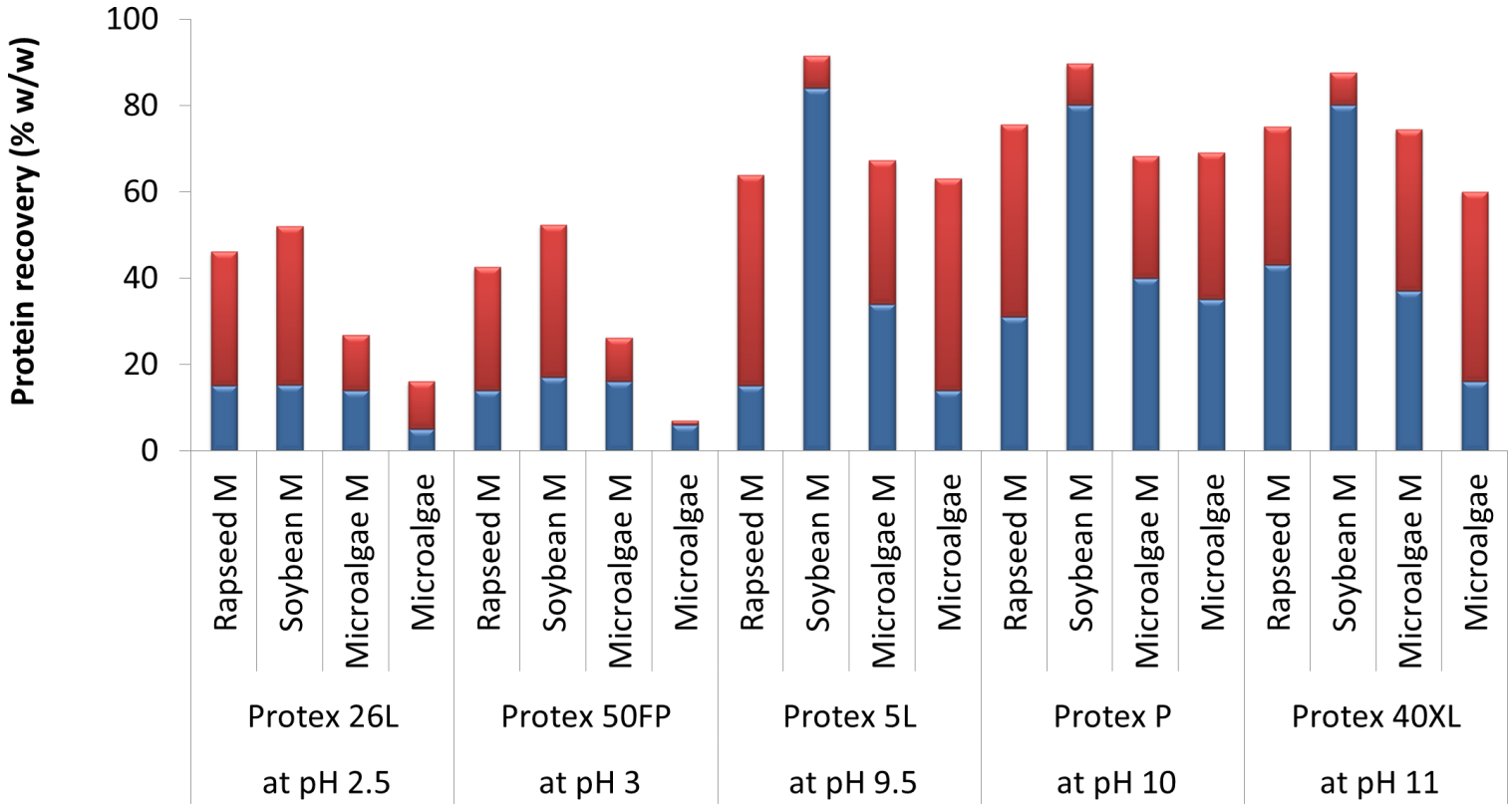


23 kton NMP

(~2500 € / ton)

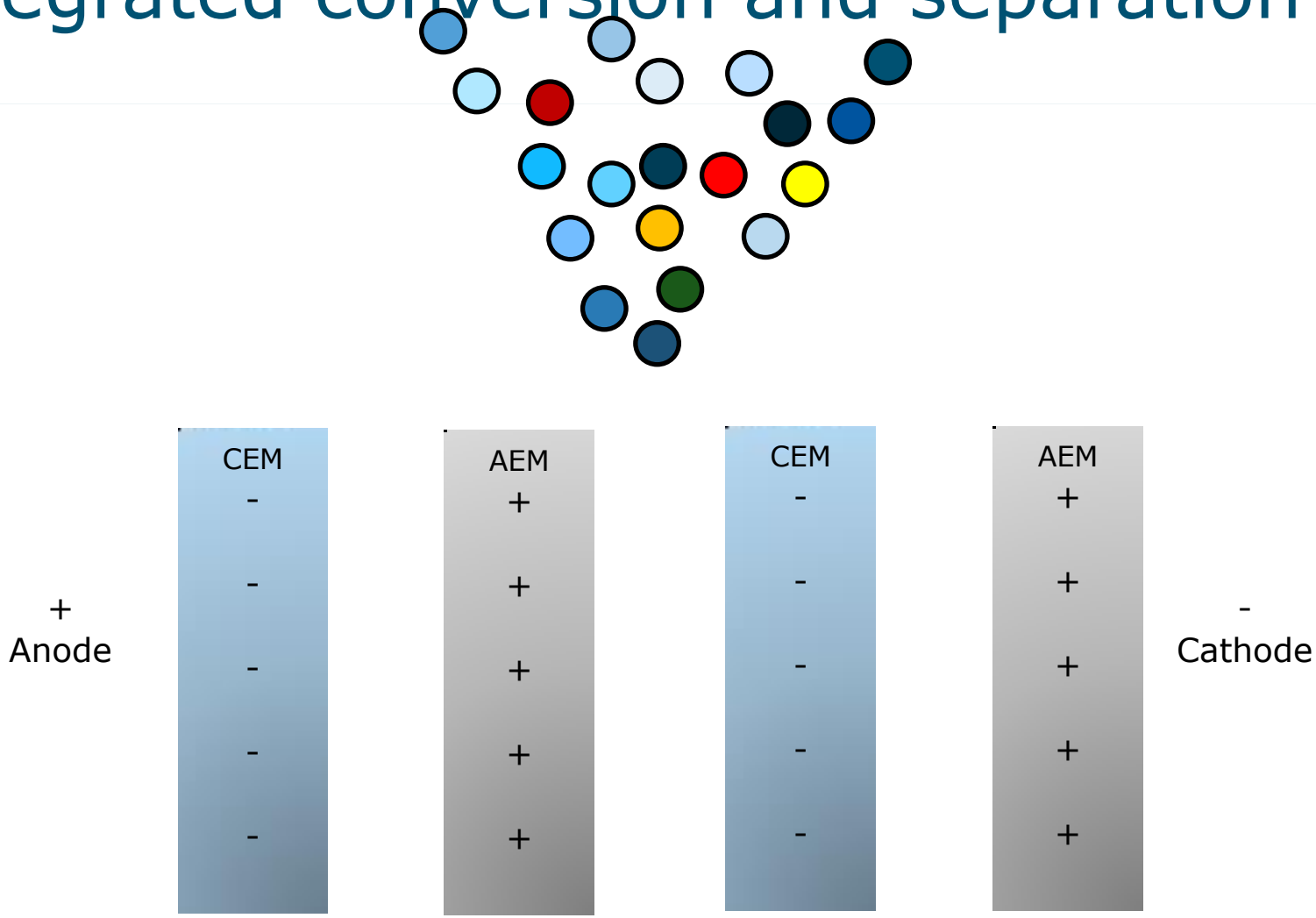
=58 M€/y

Enzymatic hydrolysis and extraction of proteins



Protein recovery after 3 hours incubation without enzymes (■) and additional by the enzymes (■) (M = meal).

Integrated conversion and separation



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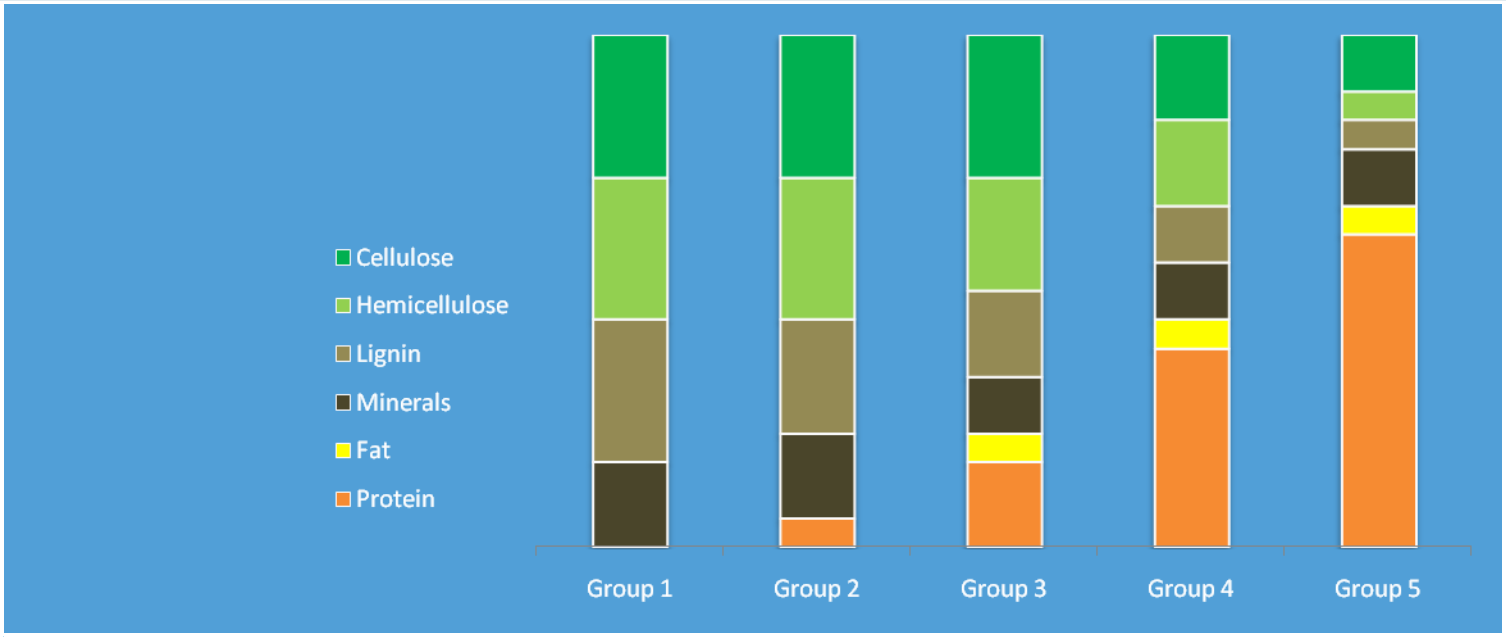
The Netherlands

Lignocellulose hydrolysate, not an ideal substrate yet

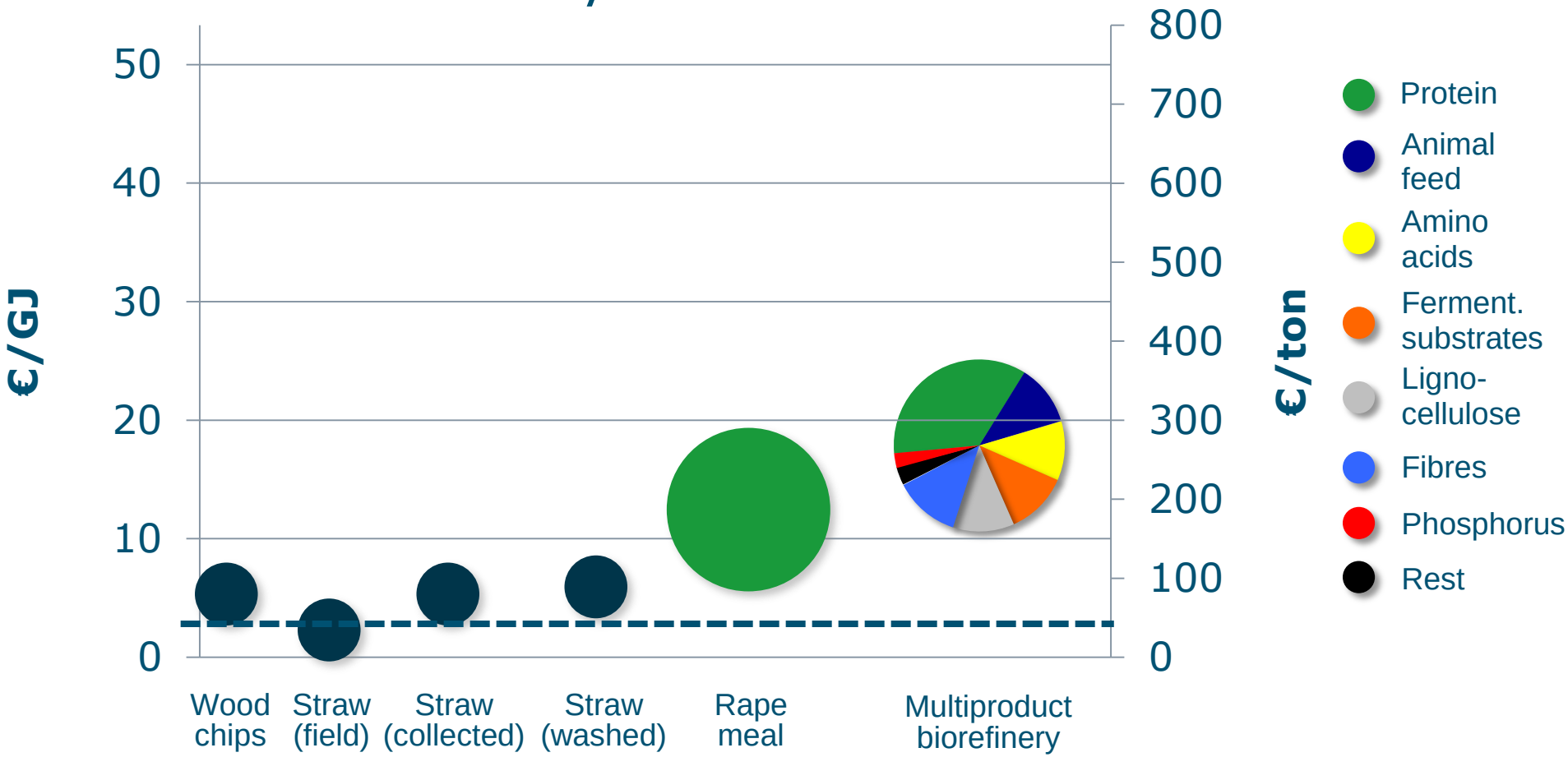
- mixing problems, low oxygen transfer, low substrate concentrations, fermentation inhibitors
- Complex: implications for product recovery

Biorefining of agricultural residues ..



Protein content	0	5 %	15 %	35 %	50 %
Examples	Wheatsstraw	cocoahulls Corncobs Sugarcane leaf	Coffee pulp Rape straw Beet leaf	Rape meal	Soy meal
Cost (€/ton)	50-80	50-110	100-140	150-180	300-350

Biorefinery enables power generation at 45€/ton and high quality 2nd generation fermentation raw materials for 200€/ ton



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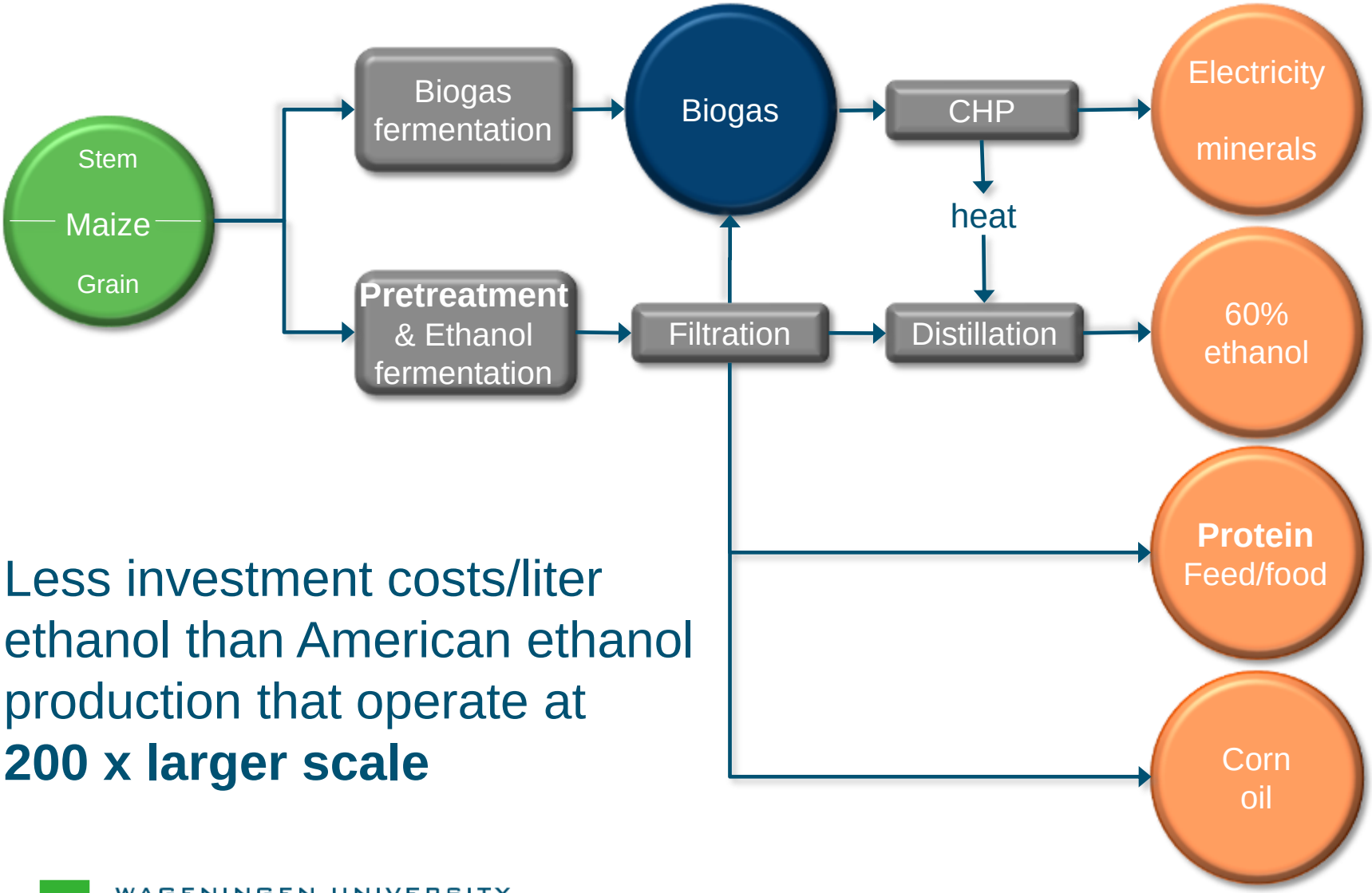
protein/oil/ethanol/biogas from small scale corn-biorefinery



Less investment costs/liter ethanol than American ethanol production that operate at **200 x larger scale**

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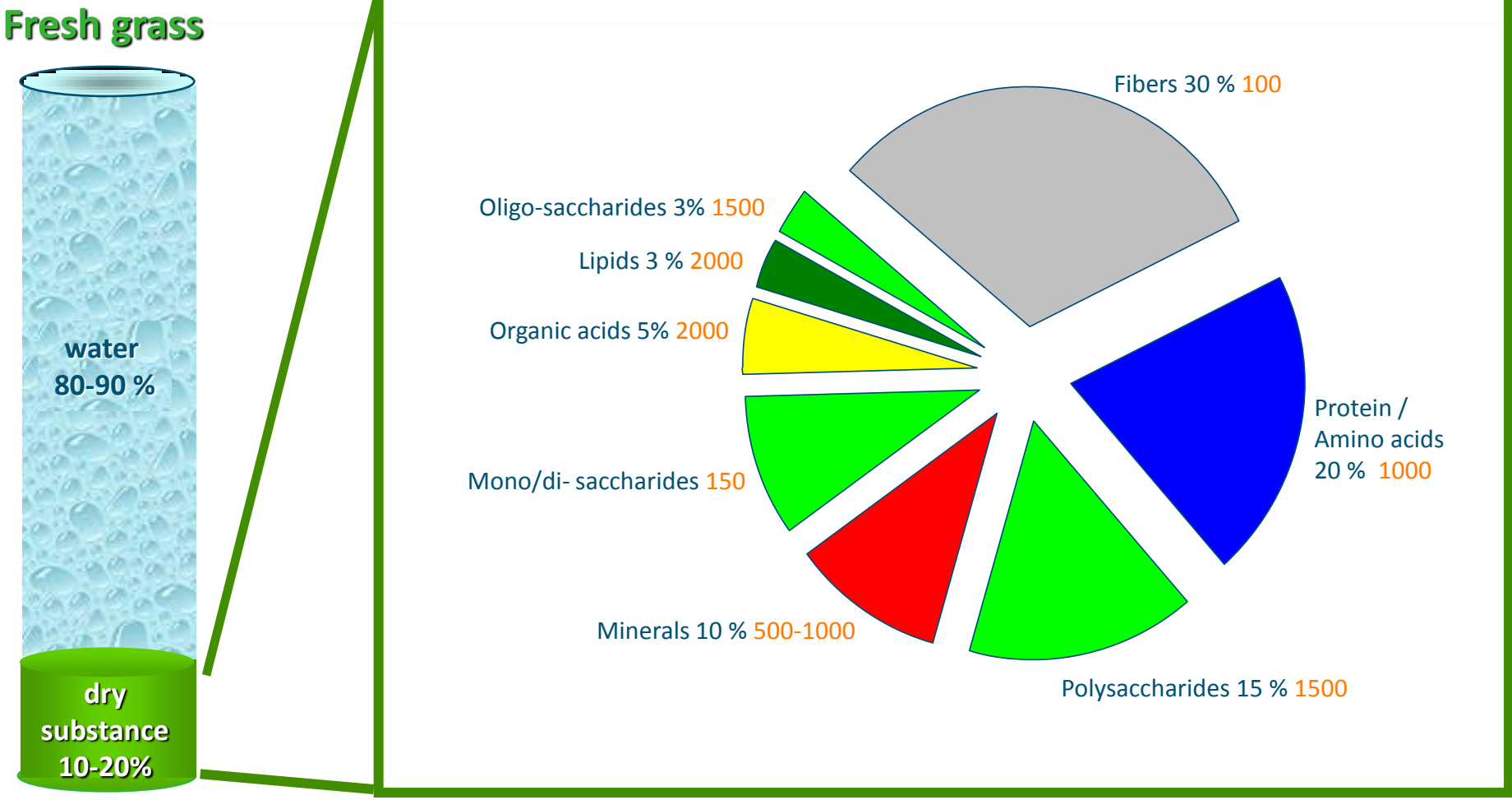
Byosis/Zeafuels (Lelystad, Netherlands)



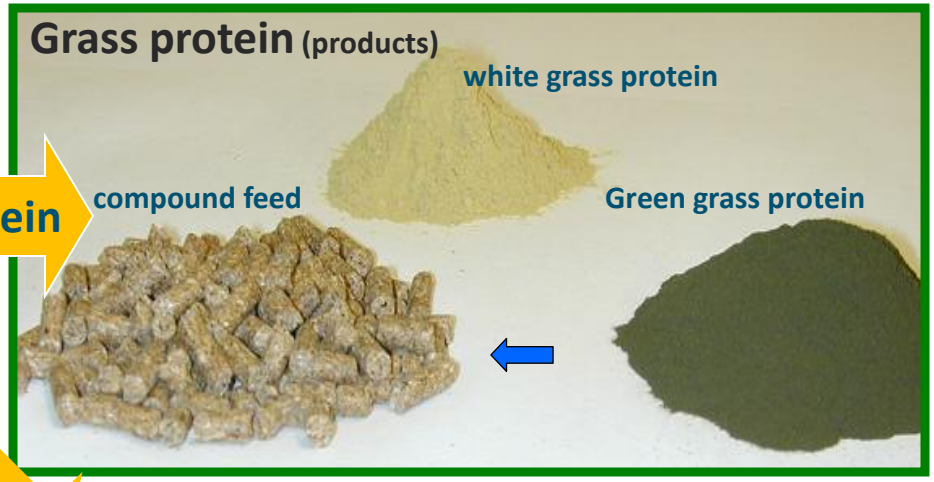



The separated components of grass value 700 – 800 €/ton as compared to 50 – 70 €/ton raw materials



Mobile grass refinery unit Grassa (the Netherlands)

Protein



Grass juice

compound feed

+ .....

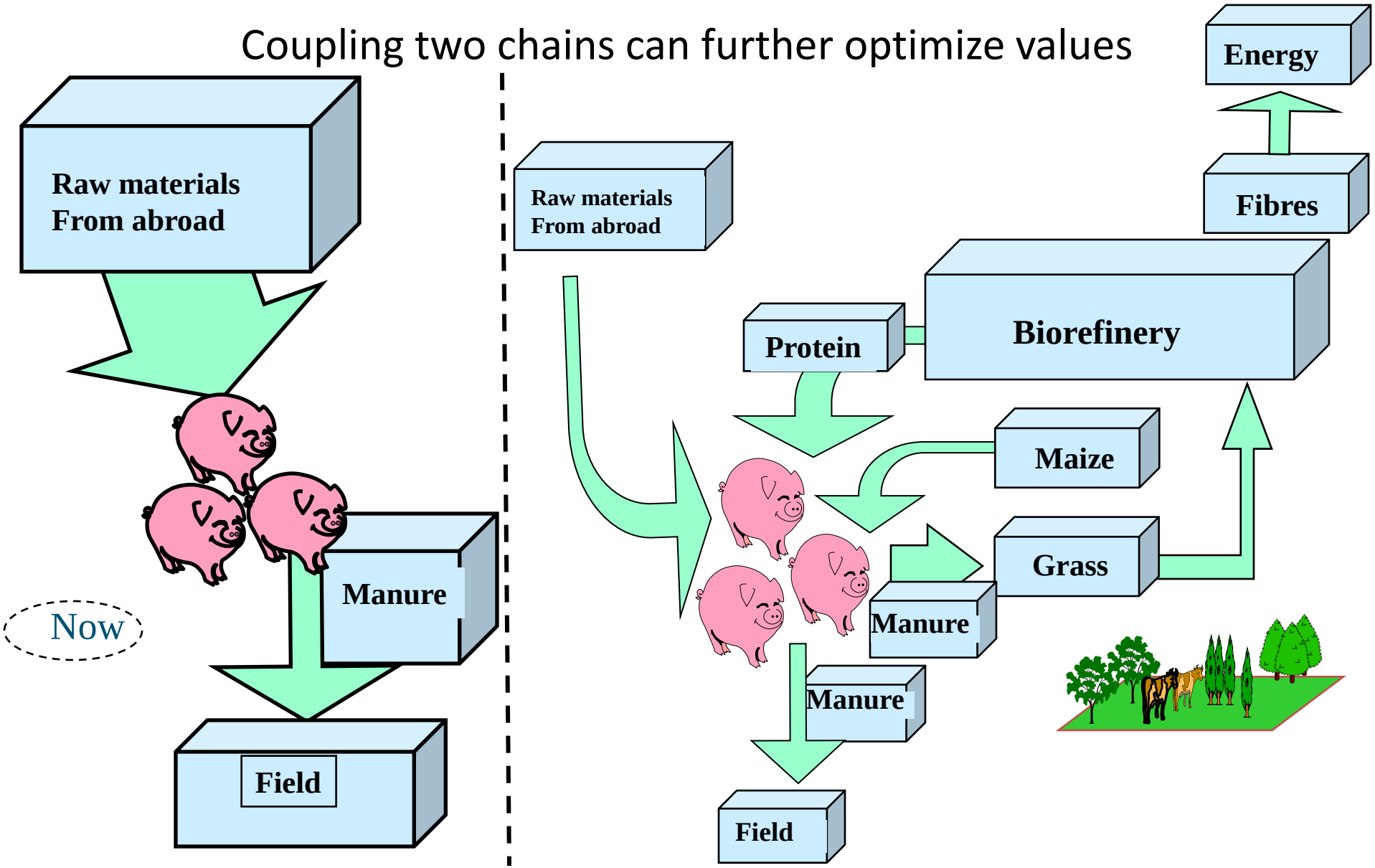
Fibers

HTU-
Biofuel

Construction
material
+ paper

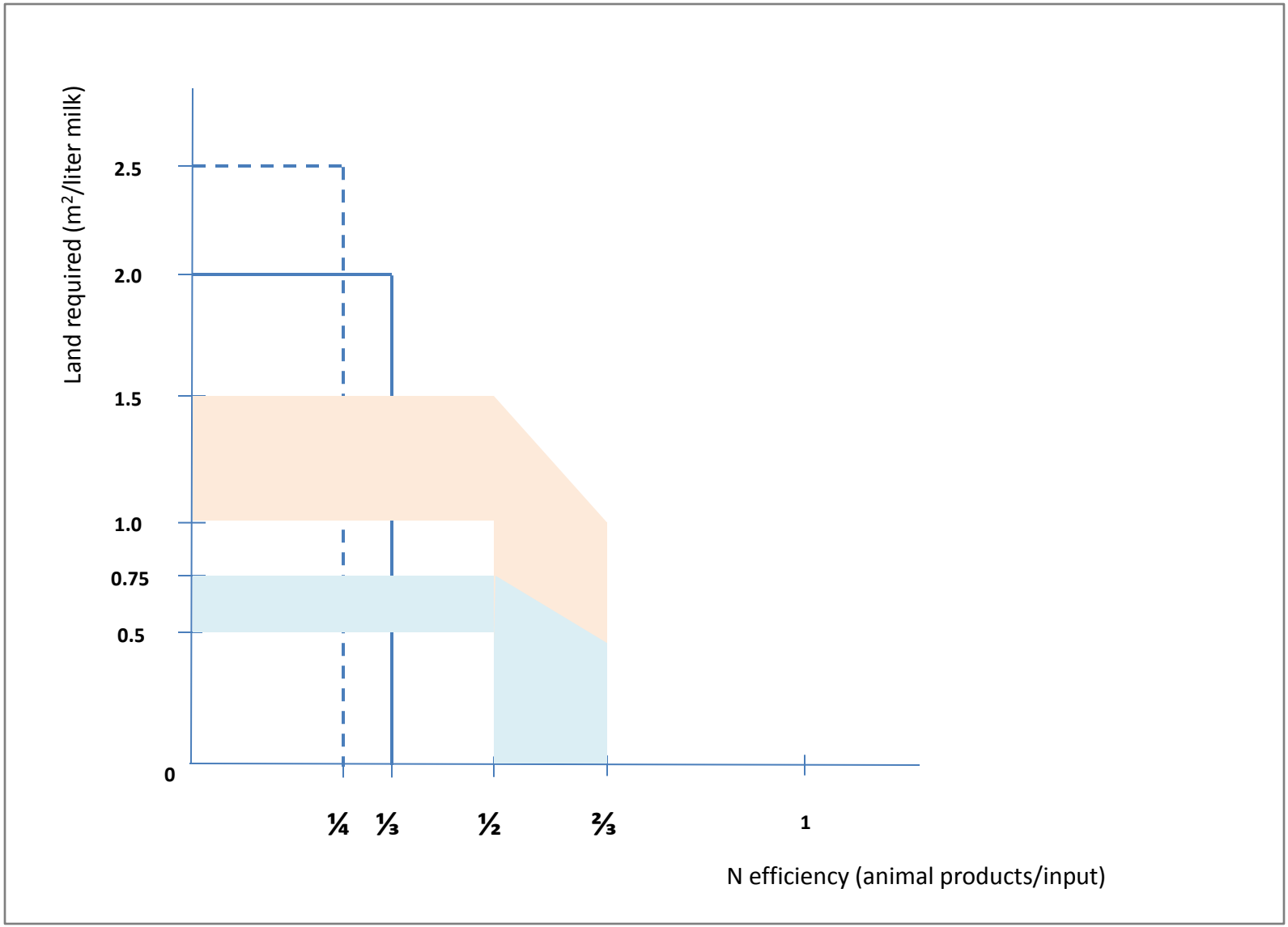
Polymer
extrusion
products

Coupling two chains can further optimize values



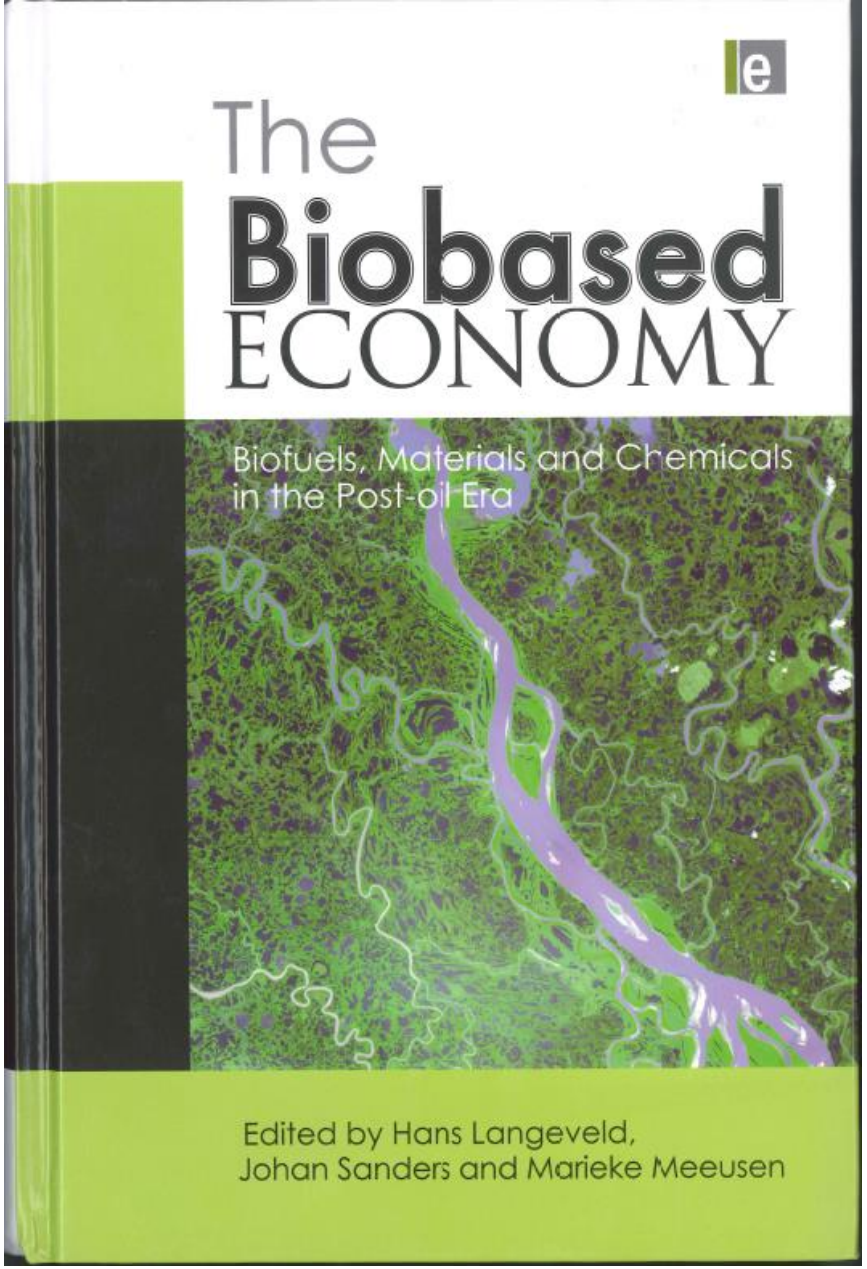
Reduction of soy import from Brazil reduces ILUC and manure problem and creates regional income

Improving N efficiency and land use



conclusions

- Use of all biomass components at their highest value enables even to compete with oil, coal and natural gas
- Use of molecular structures needs much less capital and energy
- Economy of scale is loosing its competitiveness
- Many economic ways to valorise excess of N are facilitated by the Bio based economy



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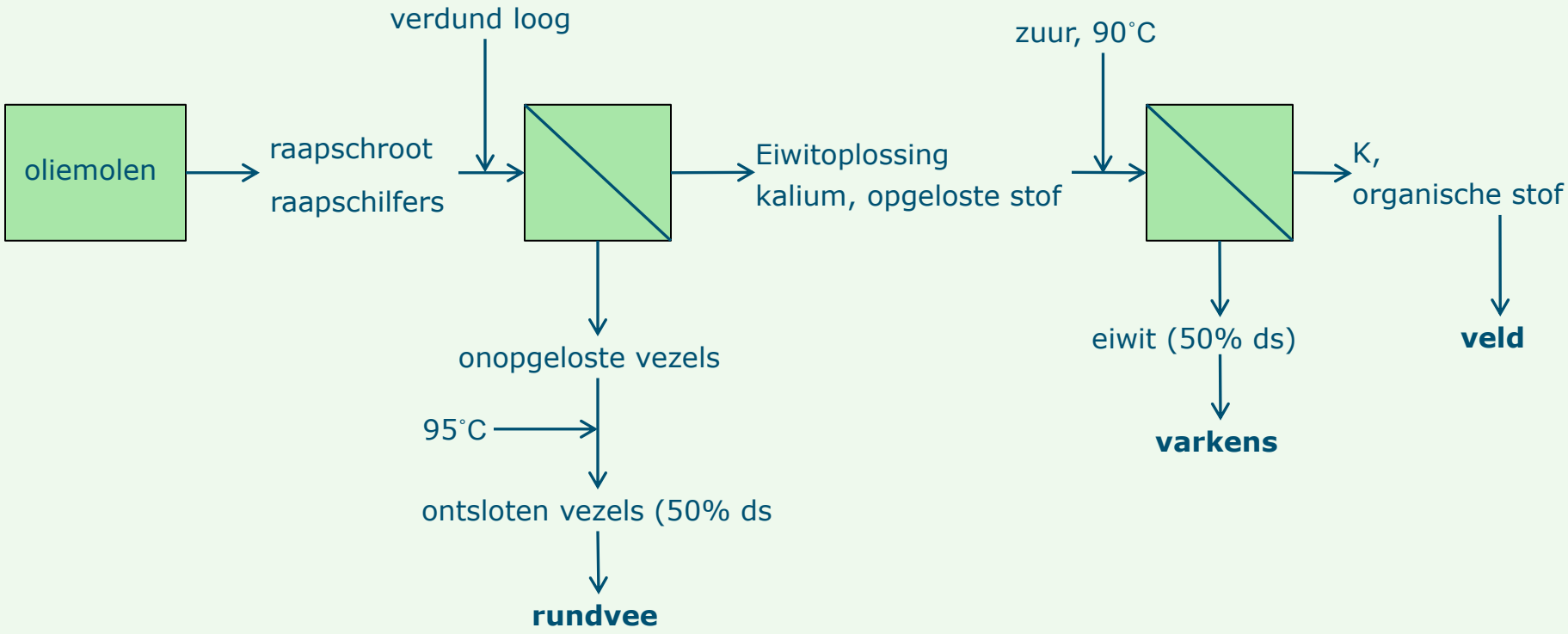
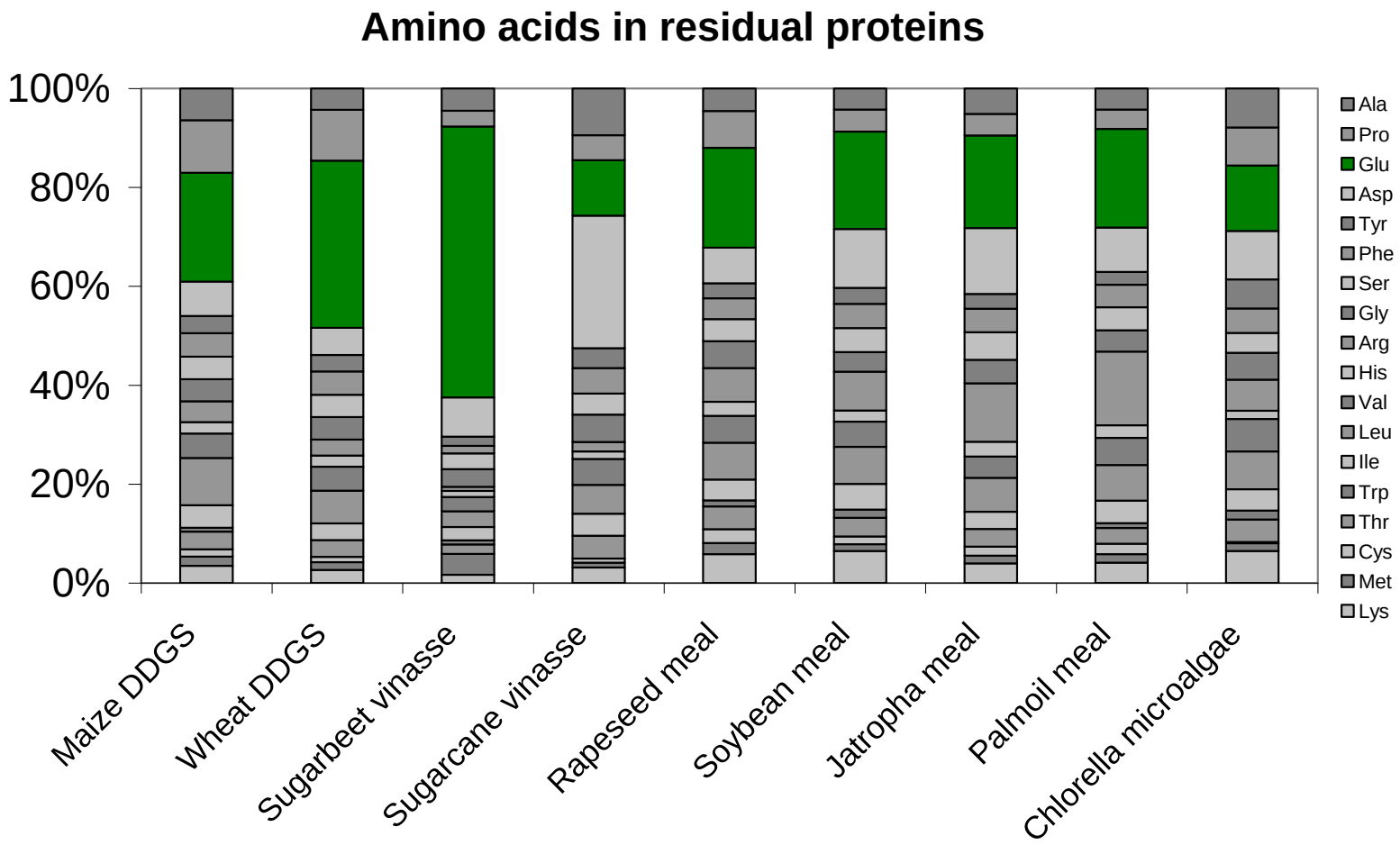
Earthscan, ISBN 978-1-84407-770-0

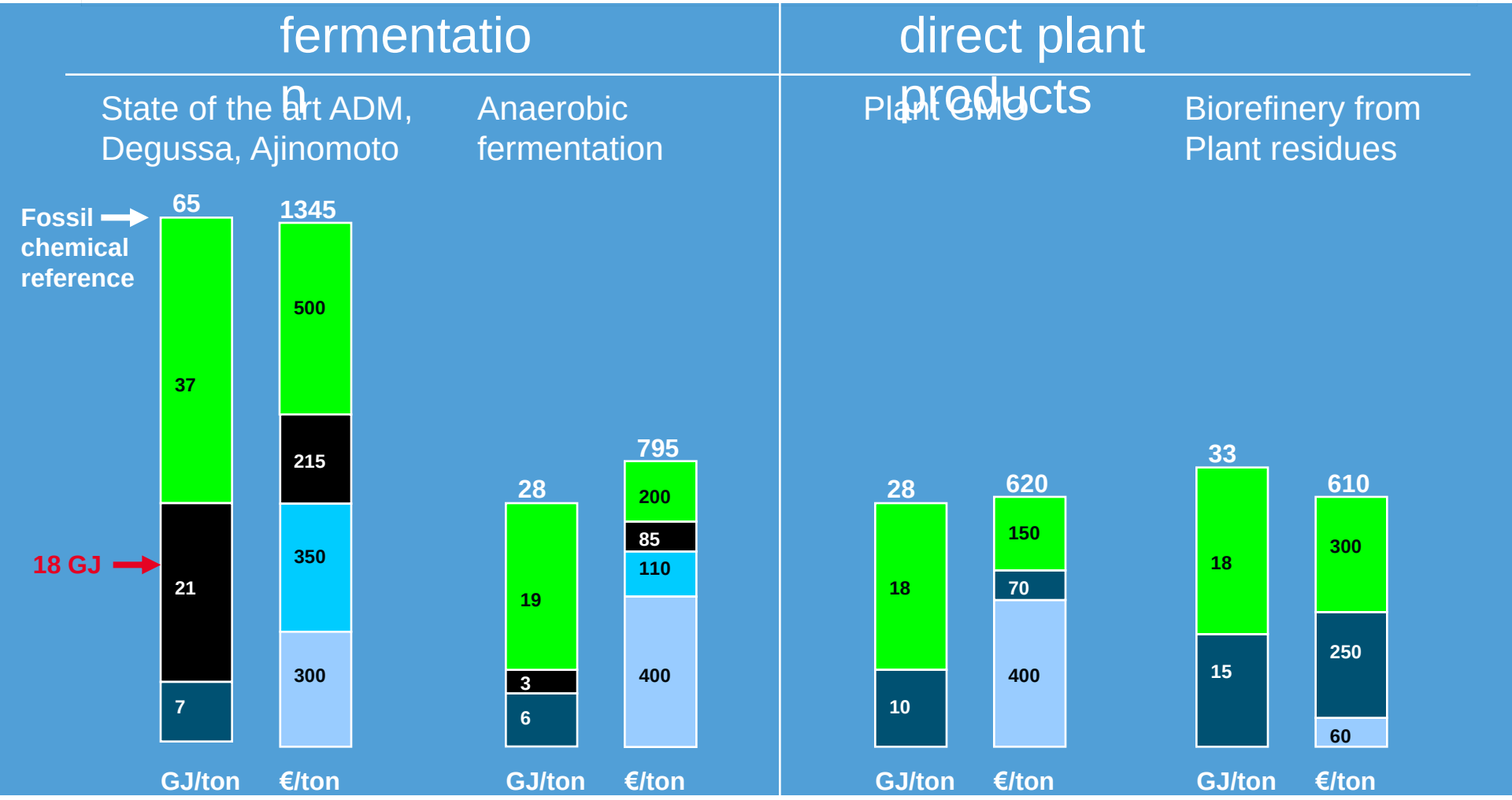
Decentrale optimalisatie van raapschilfers



Example: Glutamic acid and other aminoacids in byproduct streams



Bulk chemicals from Biomass: e.g. lysine



Fossil raw materials (fermentation)
Fossil raw materials (recovery)
Biomass raw materials
Capital (fermentation)
Capital (recovery)

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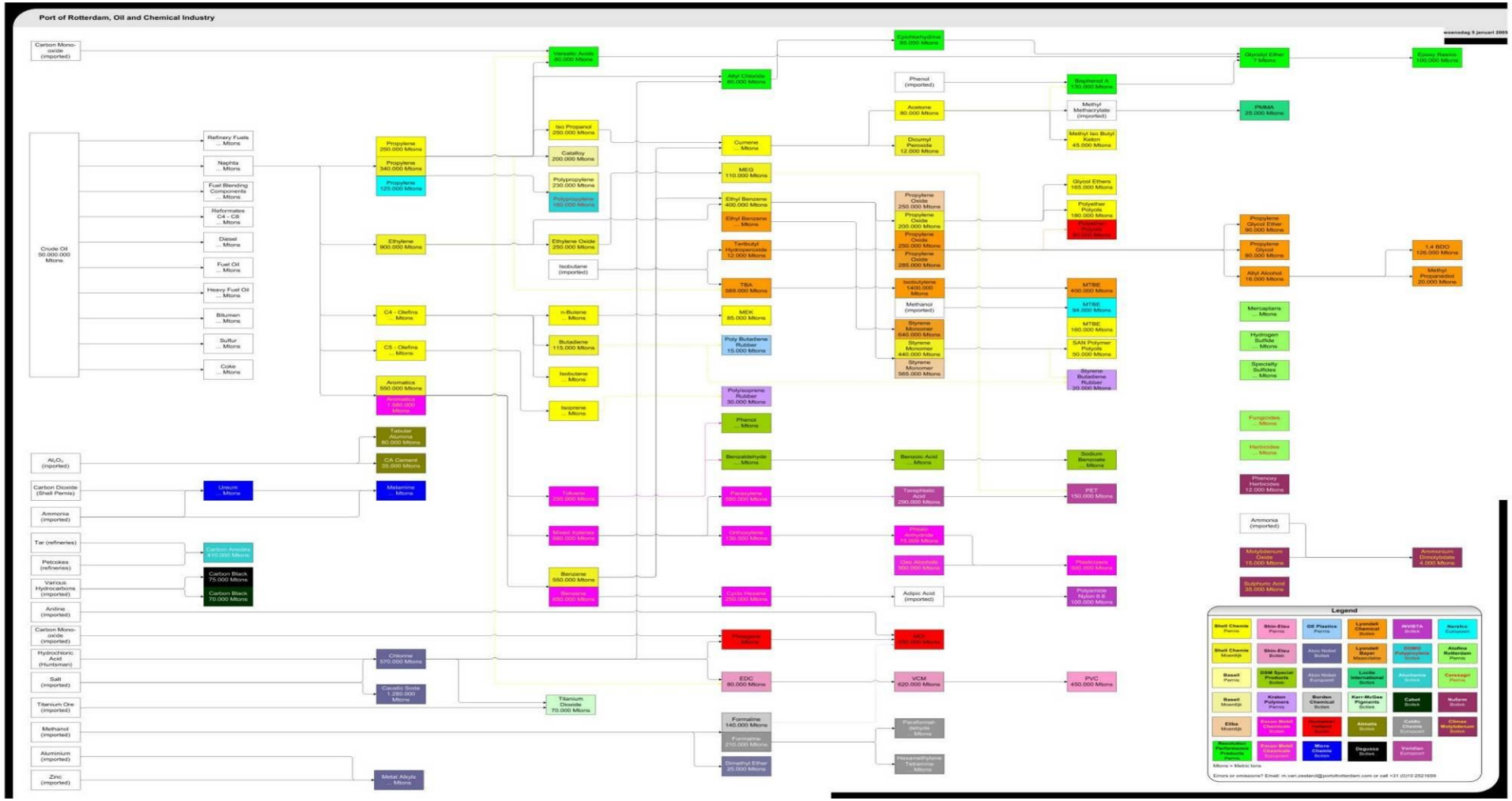
The Chemical Products of the Port of Rotterdam



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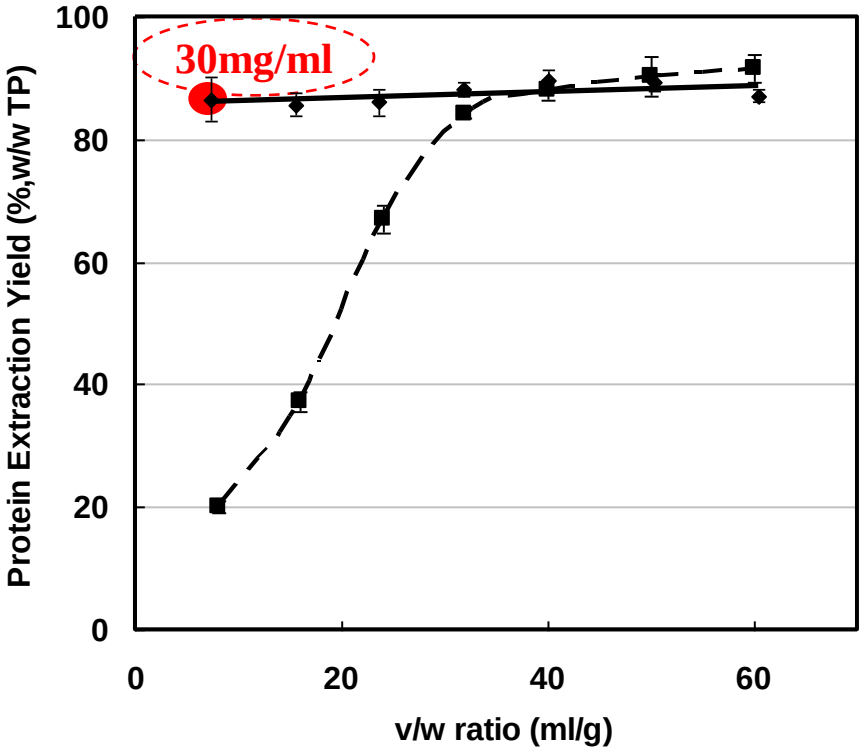
How to reduce the extraction volume?

- **Fixed volume: t: 2h; T: 95℃; Amount of NaOH: 4mmol/g**
- **Variable volume : v/w ratio**

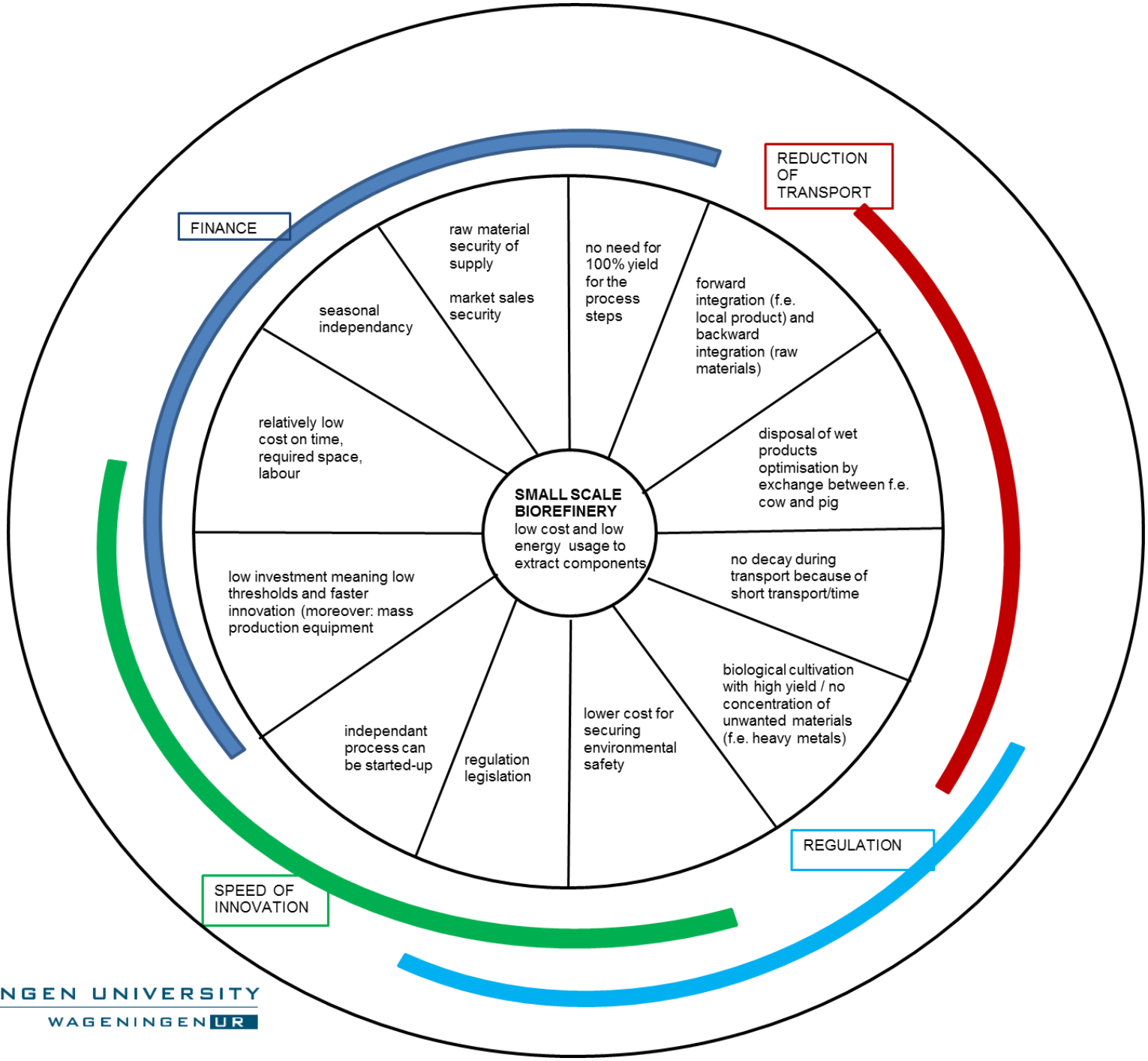
Critical parameter:
Alkaline Amount! = pH * v/w

Combination of 8ml/g with 0.4mmol/ml NaOH:

- High protein yield (>85%)
- 4 times less in heating cost
- High protein concentration (30mg/ml)
- High concentration of other constituents



--- Fixed [NaOH]
— Fixed amount of NaOH



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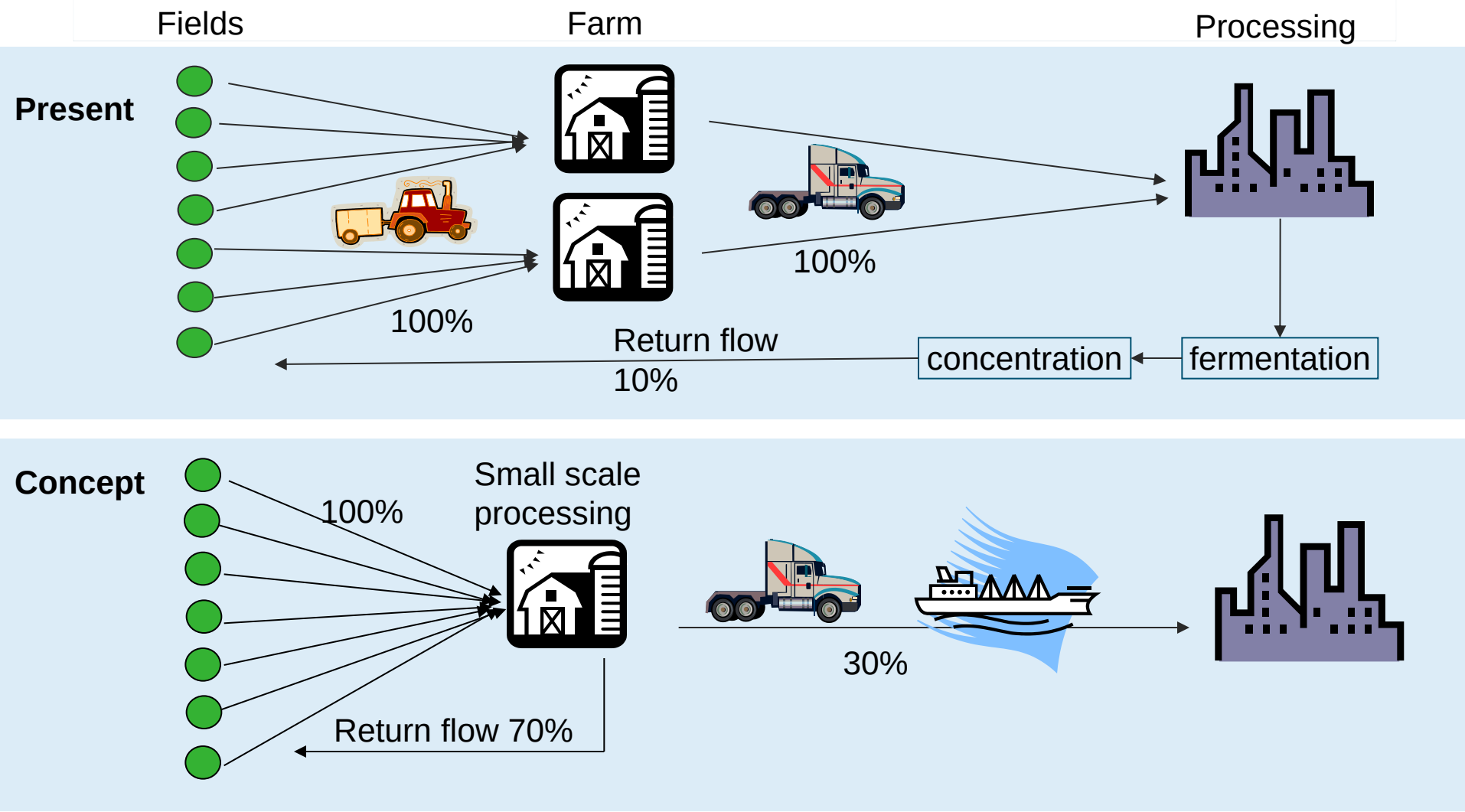
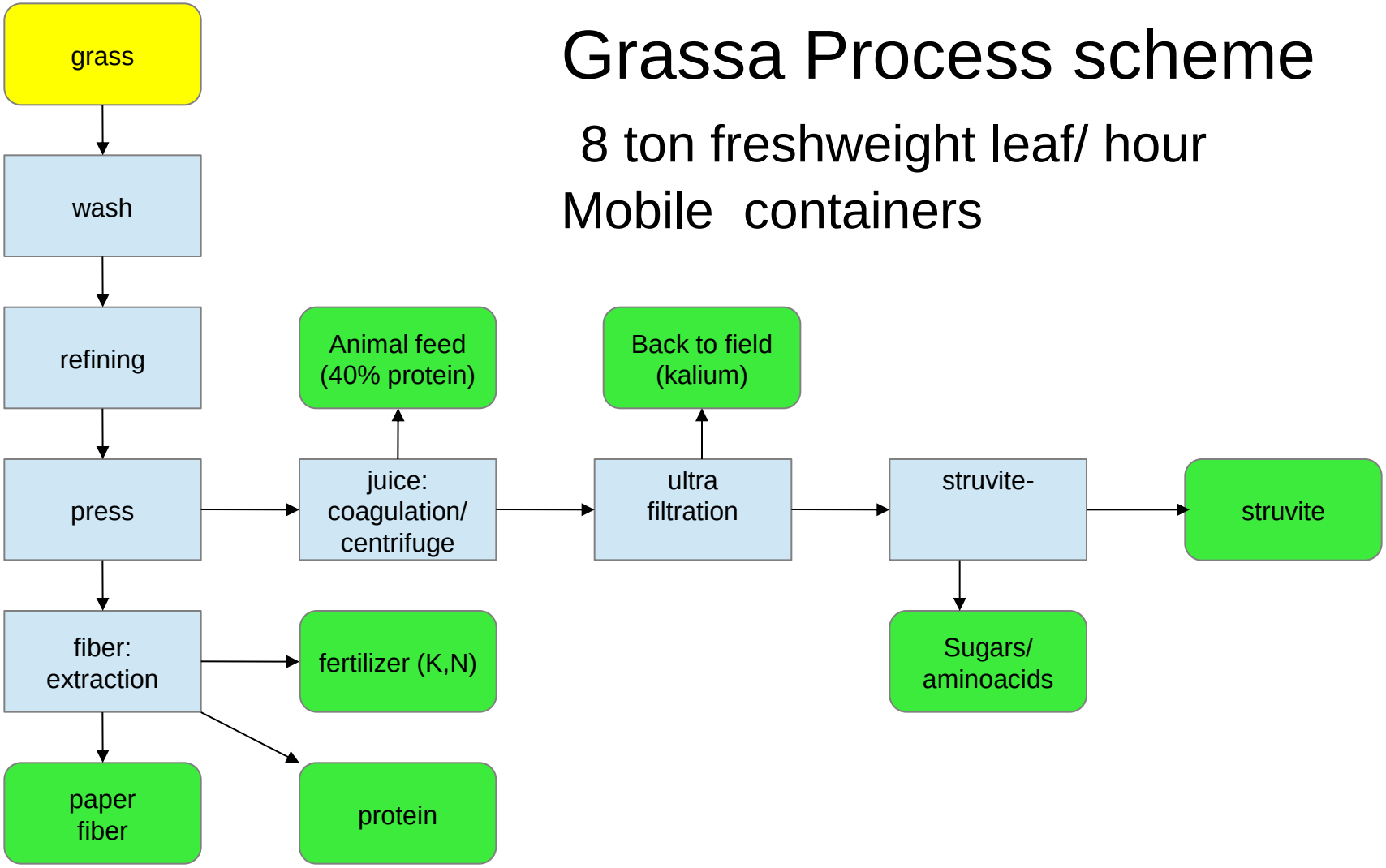
Small scale biorefinery reduces transport cost and seasonality



Grassa Process scheme

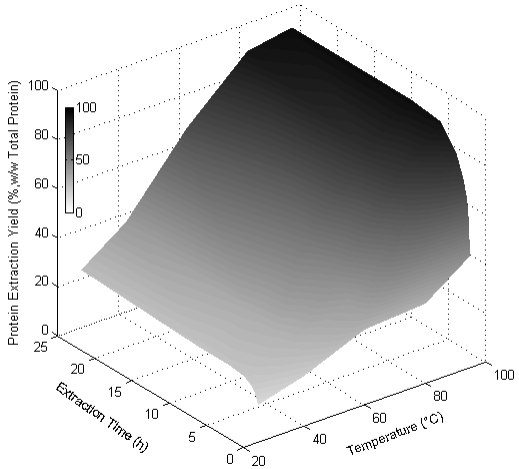
8 ton freshweight leaf/ hour

Mobile containers

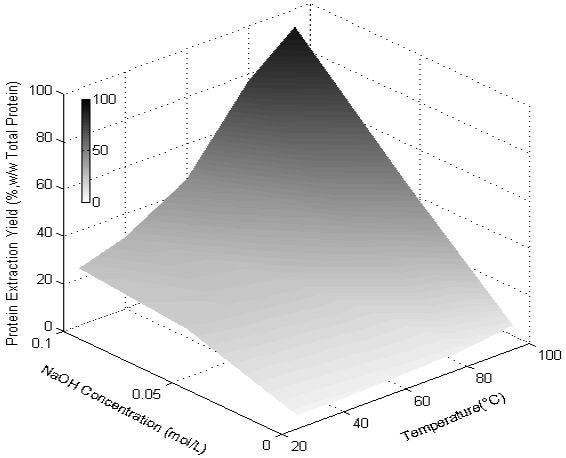


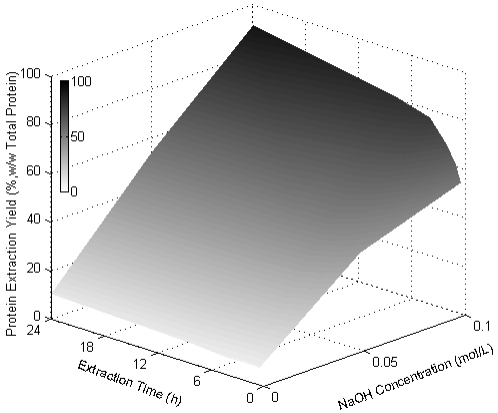
Appendix 1: Critical parameters

Tested the collective influence on protein extraction yield by fixing two parameters



- **Fixed:**
  [NaOH]: 0.1N
  v/w ratio: 40
- **Variables:**
  T(25-100 ℃)
  t (0.5-24 h)





- **Fixed:**
  T: 80 ℃
  v/w ratio: 40
- **Variables:**
  [NaOH]: 0-0.1N
  t: 0.5-24h

- **Fixed:**
  t: 4h
  v/w ratio: 40
- **Variables:**
  T: 25-100 ℃
  [NaOH]: 0-0.1N

When extraction time is longer than 2h,
Temperature and [NaOH] are critical parameters

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Economie

kosten			inkomsten		
gras+ maai/haksel+ energie	85		eiwit	135	
arbeid	42		vezel	45	
transport en droogkosten	35		fosfaat, incl ontzorg	23	
chemicals	60		sapconcentraat	50	
overig	15		meststoffen	23	
totaal	237			276	
marge	39	Payback time		3.2	jaar
capaciteit	8000	ton/jaar	investering	1000000	
absolute marge	312000	€/jaar			

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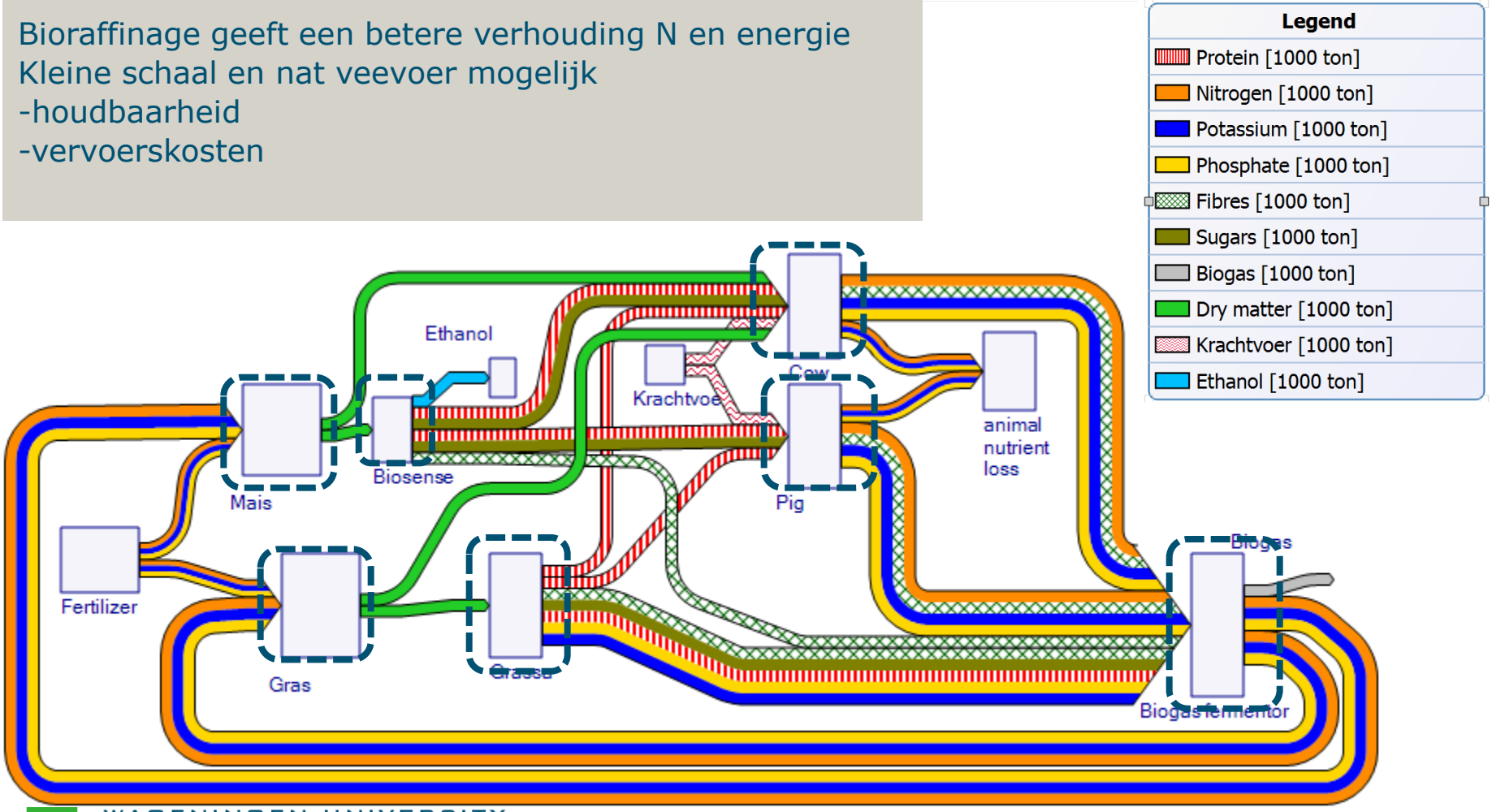
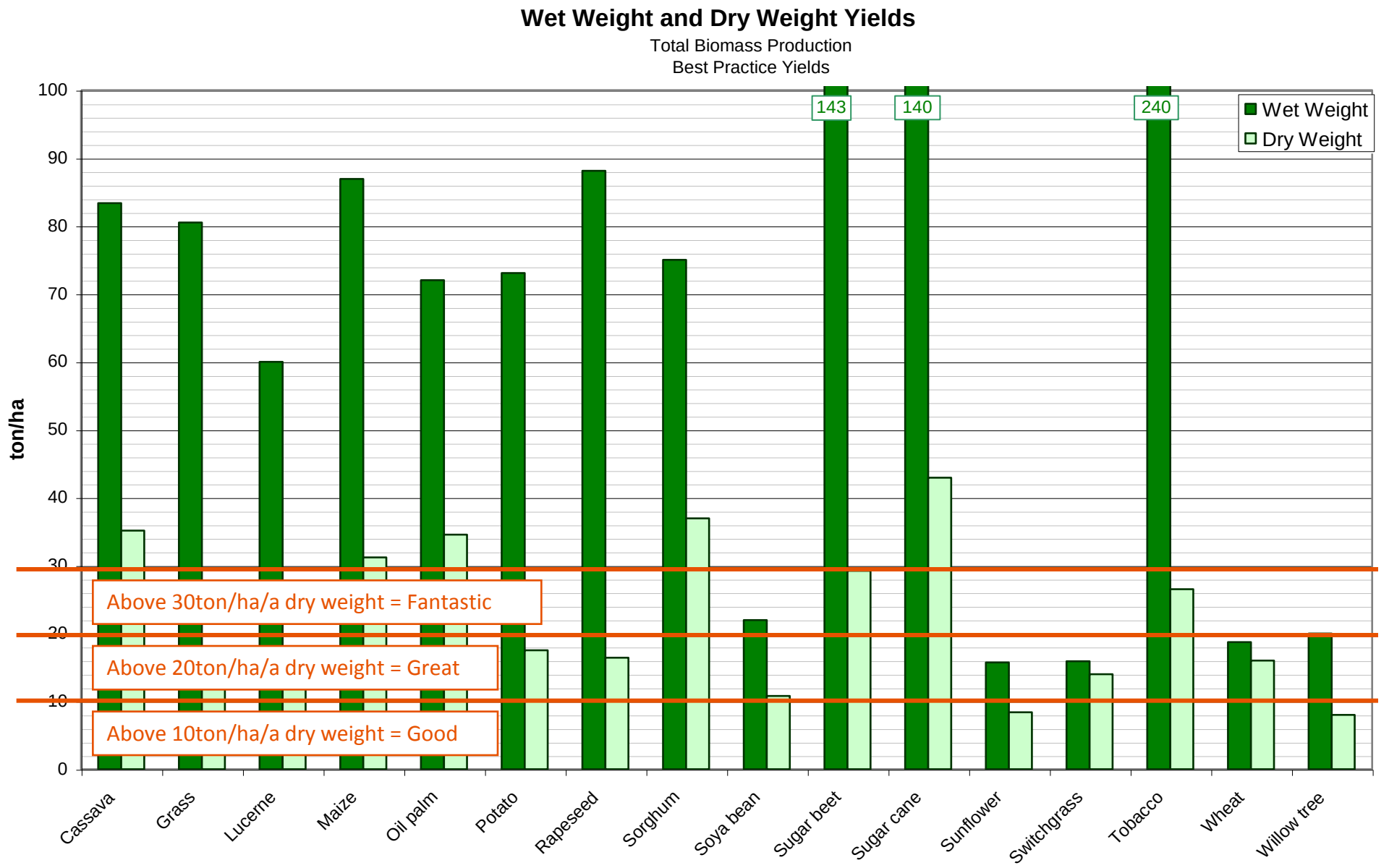
Achterhoek produceert eigen diervoeder uit gras en mais en reduceert mestpobleem

Maak eigen eiwit rijk veevoer i.p.v. soja import

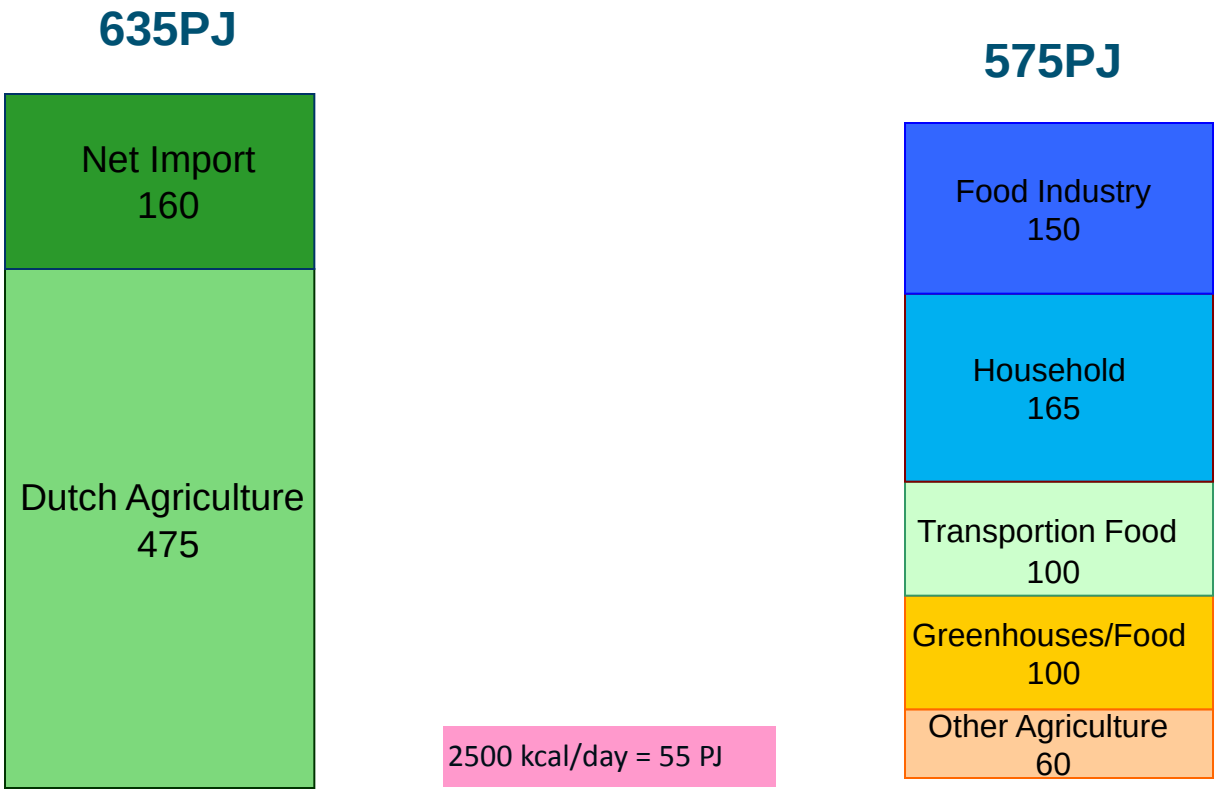
Bioraffinage geeft een betere verhouding N en energie
Kleine schaal en nat veevoer mogelijk
-houdbaarheid
-vervoerskosten



Total crop yields

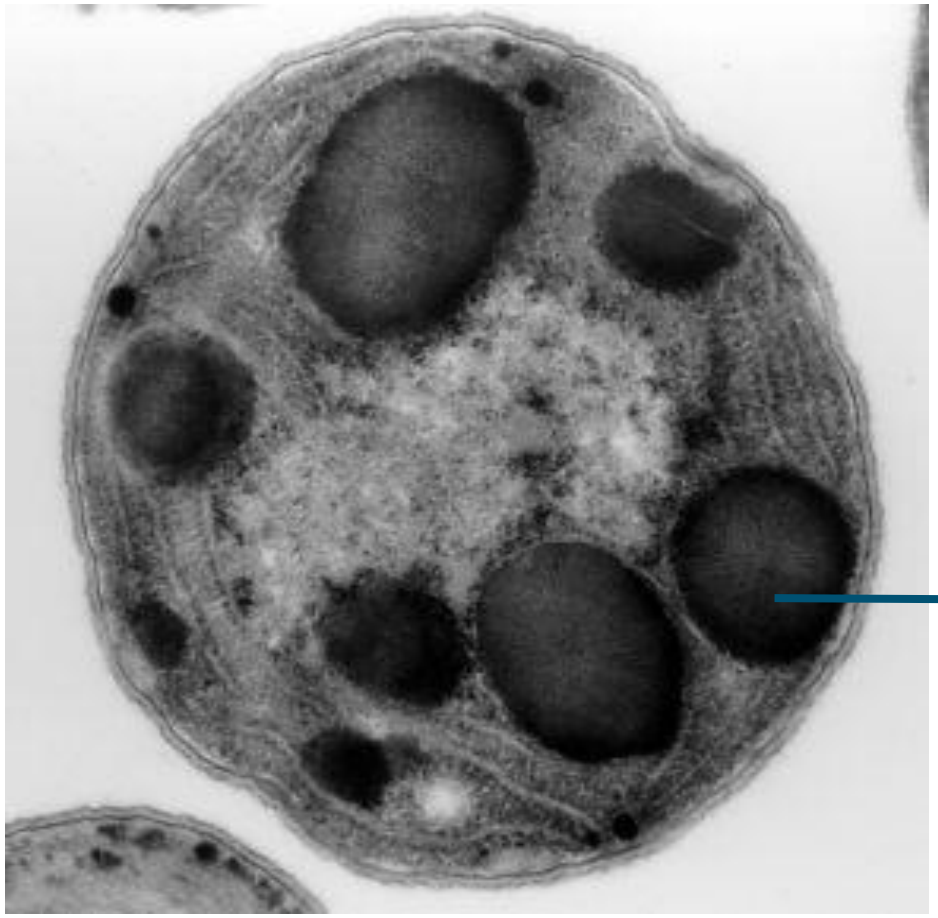


Our daily food needs a twenty fold higher energy input



2500 kcal/day = 55 PJ

Ethanol and Cyanophycin building blocks from yeast: two products for the price of one

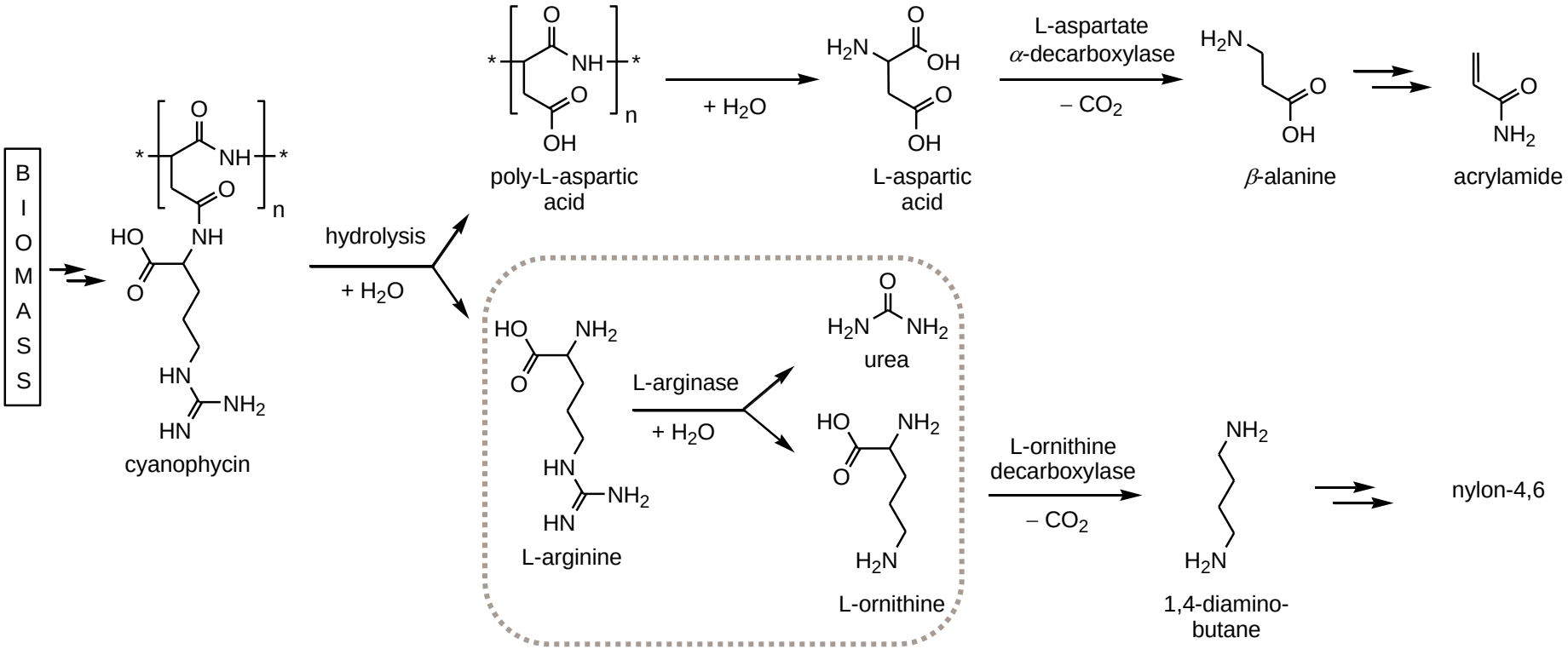


Cyanophycin mainly in cyanobacteria as nitrogen and energy reserve material

= Asp + Arg

Granule
35% (wt/wt) and slow growth

N-chemicals from cyanophycin



Focus:

- cyanophycin hydrolysis
- α-decarboxylation of L-aspartic acid
- L-arginine hydrolysis
- L-ornithine decarboxylation