Åbo Akademi

HIGH PRESSURE PROCESSES

Universidad de Valladolid

High-pressure technology in the processing of biomass

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hpp.uva.es

0 what society needs

NEEDS - PROBLEMS

SOLUTIONS

MEDICINS AND DRUGS

TRANSPORTS and FUELS

COMUNICATIONS and COMPUTERS

PESTICIDES and FERTILIZERS

CLEANING and DISINFECTION PRODUCTS

EXPLOSIVES

PACKAGING and CONTAINERS…

WELFARE STATE - WELLBEING

Is it sustainable?

0

what society needs

ECONOMY

PRODUCTS

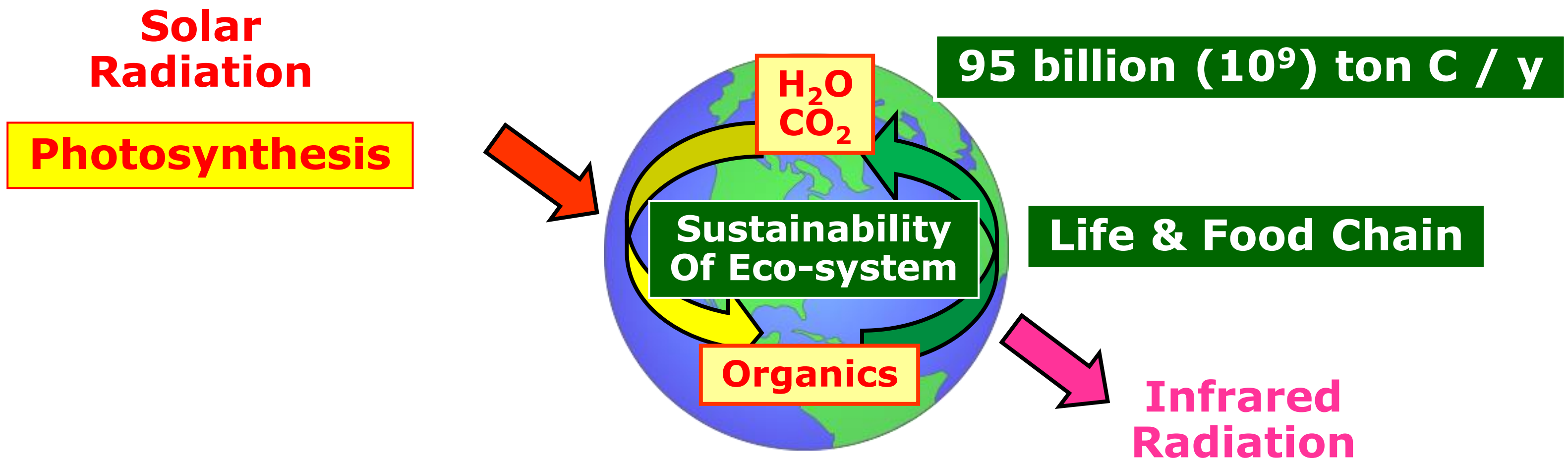
SERVICES

MATERIAL

ENERGY

WORK

1 bioeconomy paradigm



Man is a part of the eco-system

The only answer to a sustainable society is

to establish Material Recycle driven by solar energy that is harmonized with the eco-system.

2 energy options

PETROLEUM

CARBON

ETC...

SHALE GAS

GAS

2

energy options

Biomass circulation by Photosynthesis

95 billion (10^9) ton C/y

>

Present world consumption of Fossil Fuel

6.5billion (10^9) ton C/y

Independence from fossil fuels can be achieved by using less than **10%** of this circulating Biomass

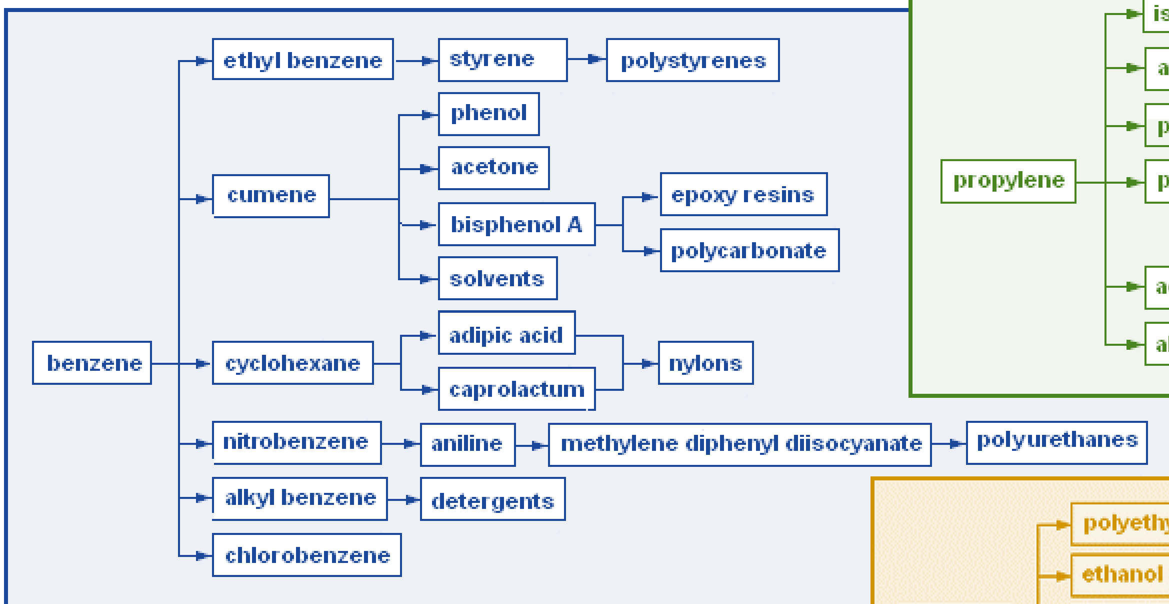
A Fundamental Sustainable Society Driven by an External Energy can be achieved

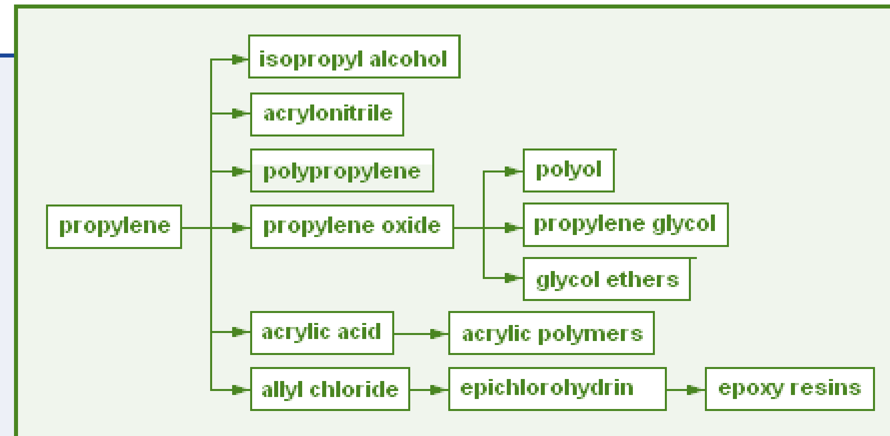
Determining the Sustainable limit of harvest is an important task of the future.

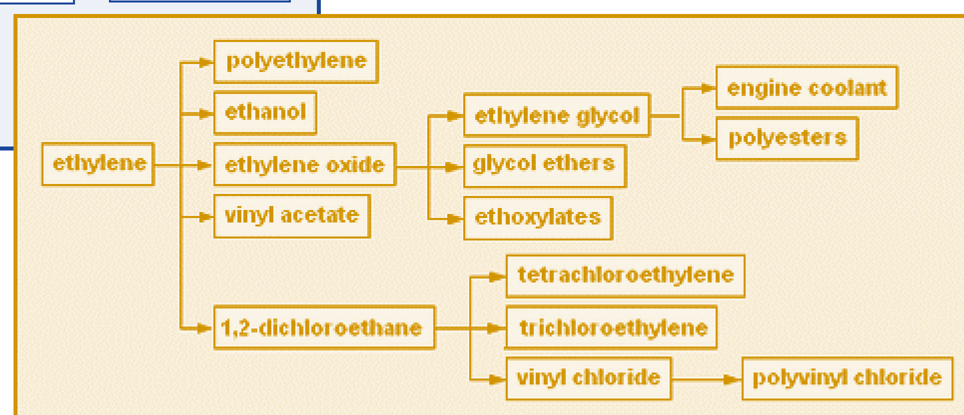
3 raw material options

PETROLEUM

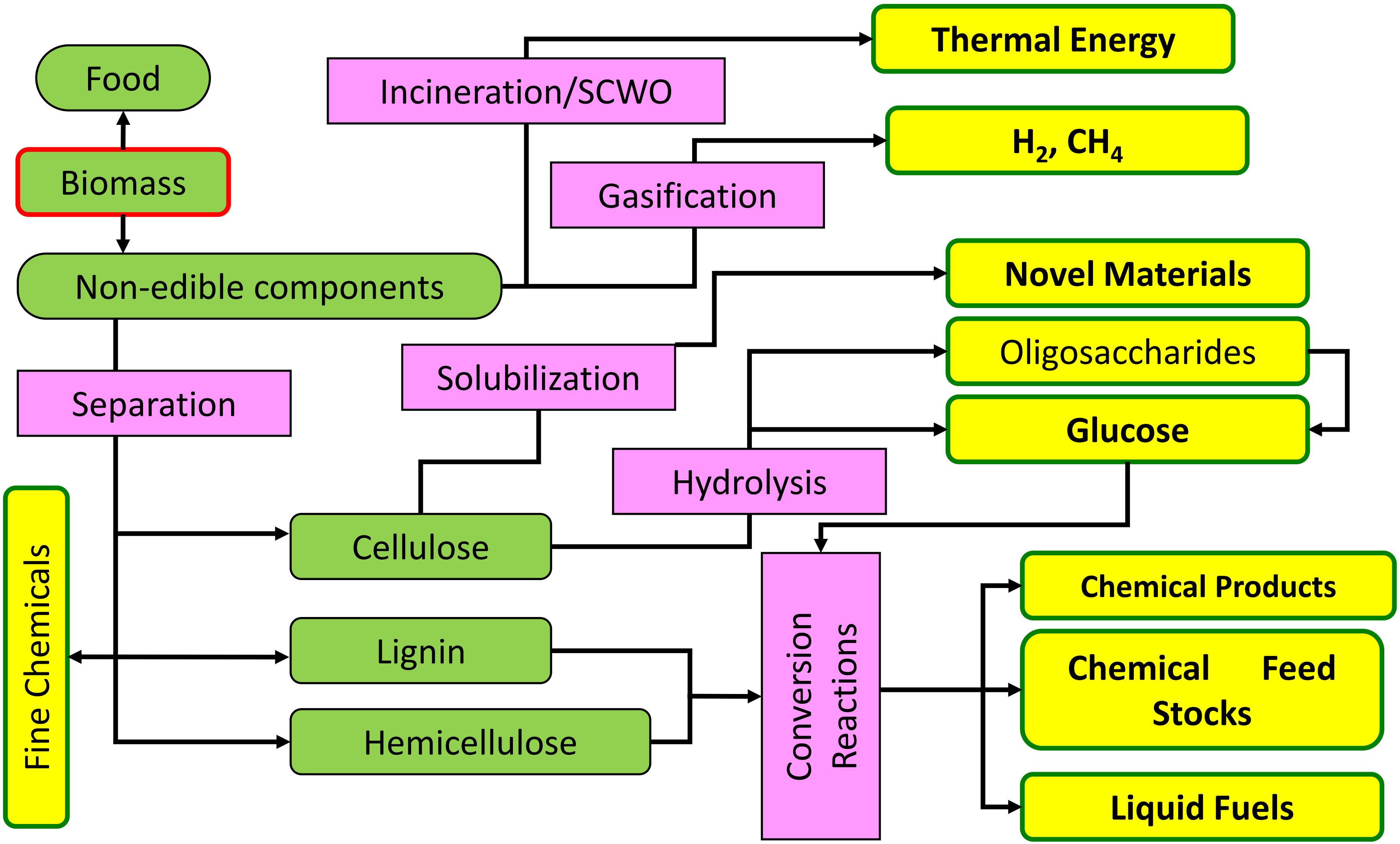
GAS







3 raw material options



4 biomass, of course !!

4 biomass – biofuels generations

1st GENERATION

CORN, SOYA…

VEGE OIL

2nd GENERATION

RESIDUES

LIGNOCELLULOSICS

3rd GENERATION

MICRO ALGAE

4th GENERATION

PETROLEUM-LIKE HYDROPROCESS

BIOCHEMISTRY

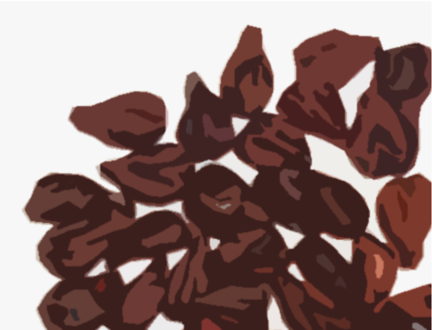
SOLAR-TO-FUEL

4

biomass (2ª G)

GRAPE SEED

POLYPHENOLS	< 1%
ESSENTIAL OIL	< 12-15%
HEMICELLULOSE	< 15-25%
CELLULOSE	< 25-35%
LIGNIN	< 35%
ASHES	< 2-3%



4 biomass (wood)

SOFTWOOD

(gimnosperms)

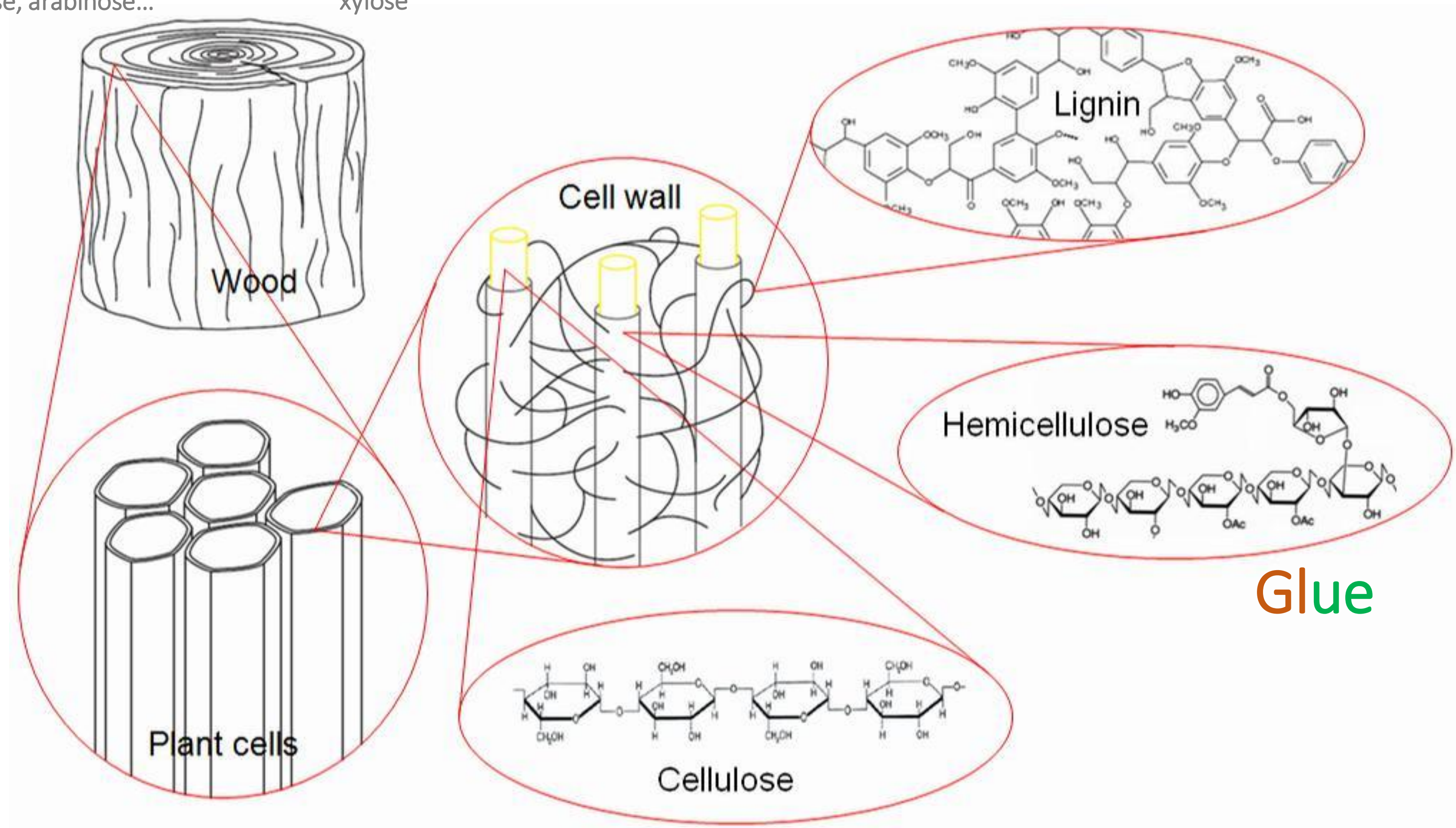
Manose, arabinose...

HARDWOOD

(angiosperms)

xylose

Structura 3D

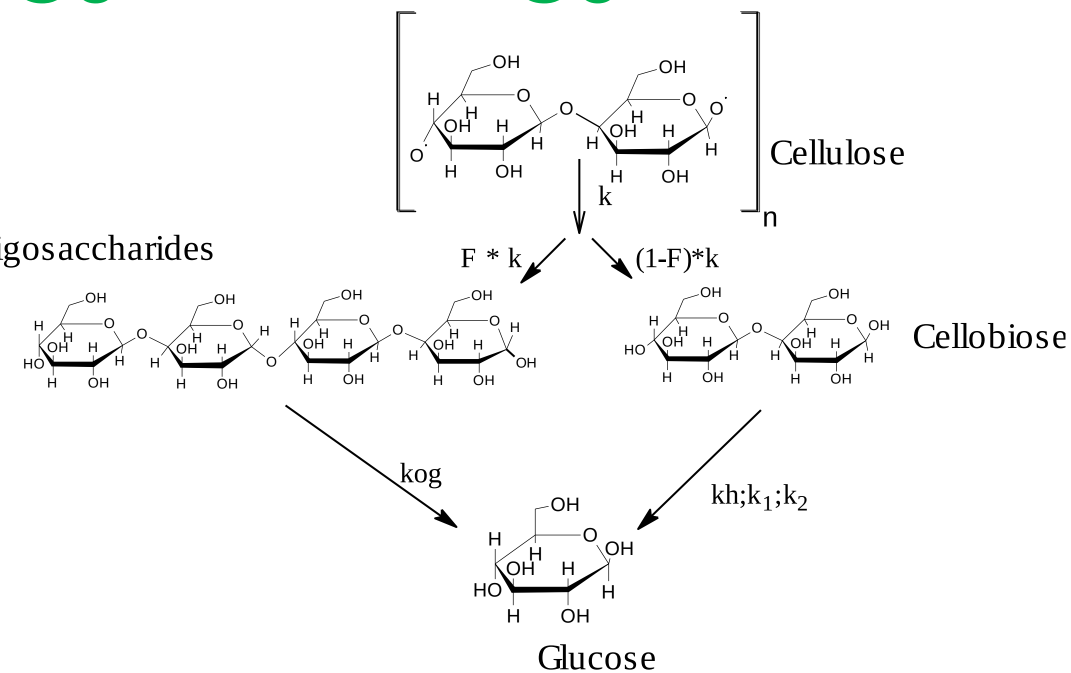


Glue

Fibbers

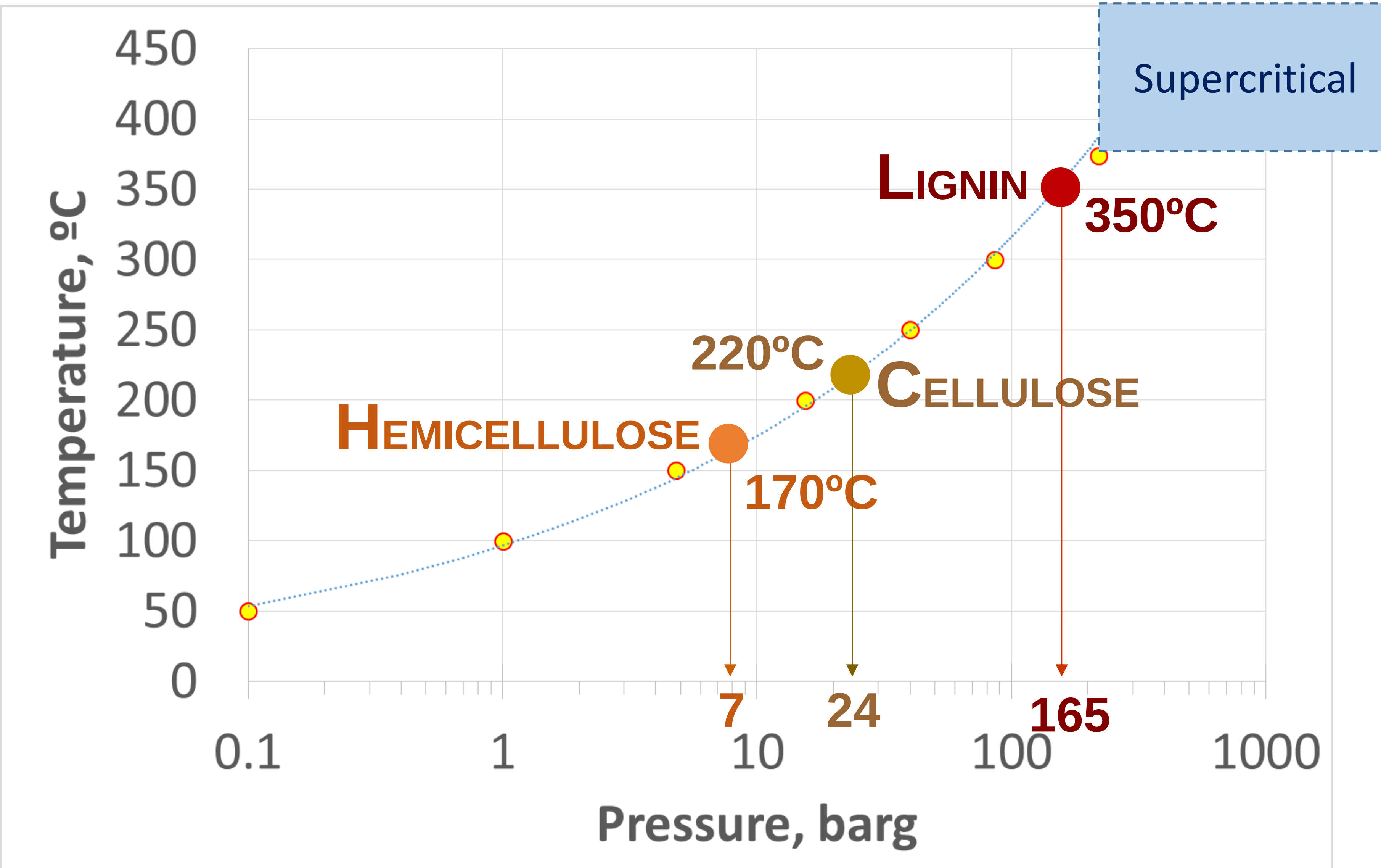
4 biomass

Glue	Fibbers	Structura 3D
HEMICELLULOSE	**CELLULOSE**	**LIGNIN**
↓	↓	↓
C5 C6	**C6**	**Aromatics**



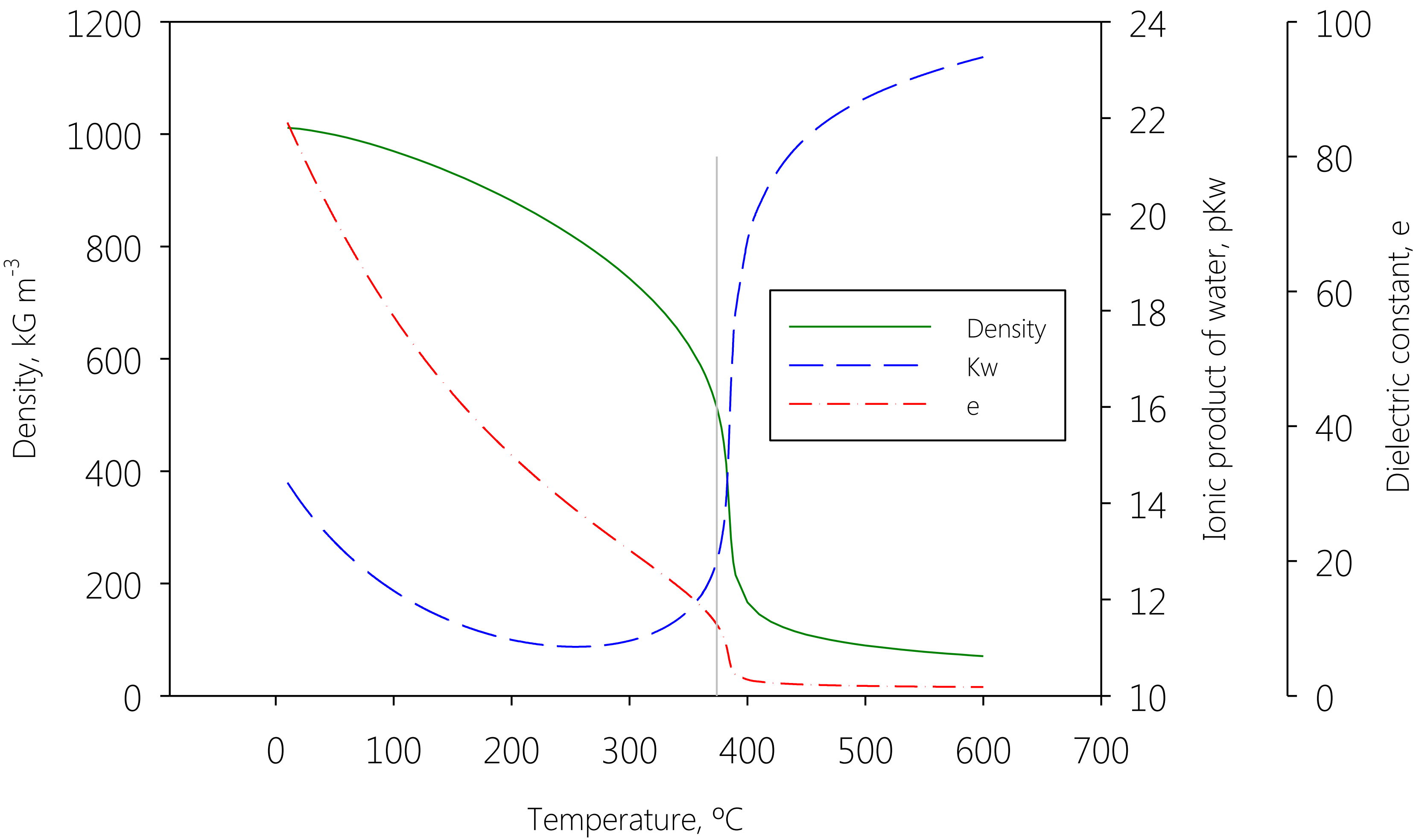
5

phase equilibria - water



5 supercritical fluids - water

Tc=374ºC   Pc=22.1 MPa



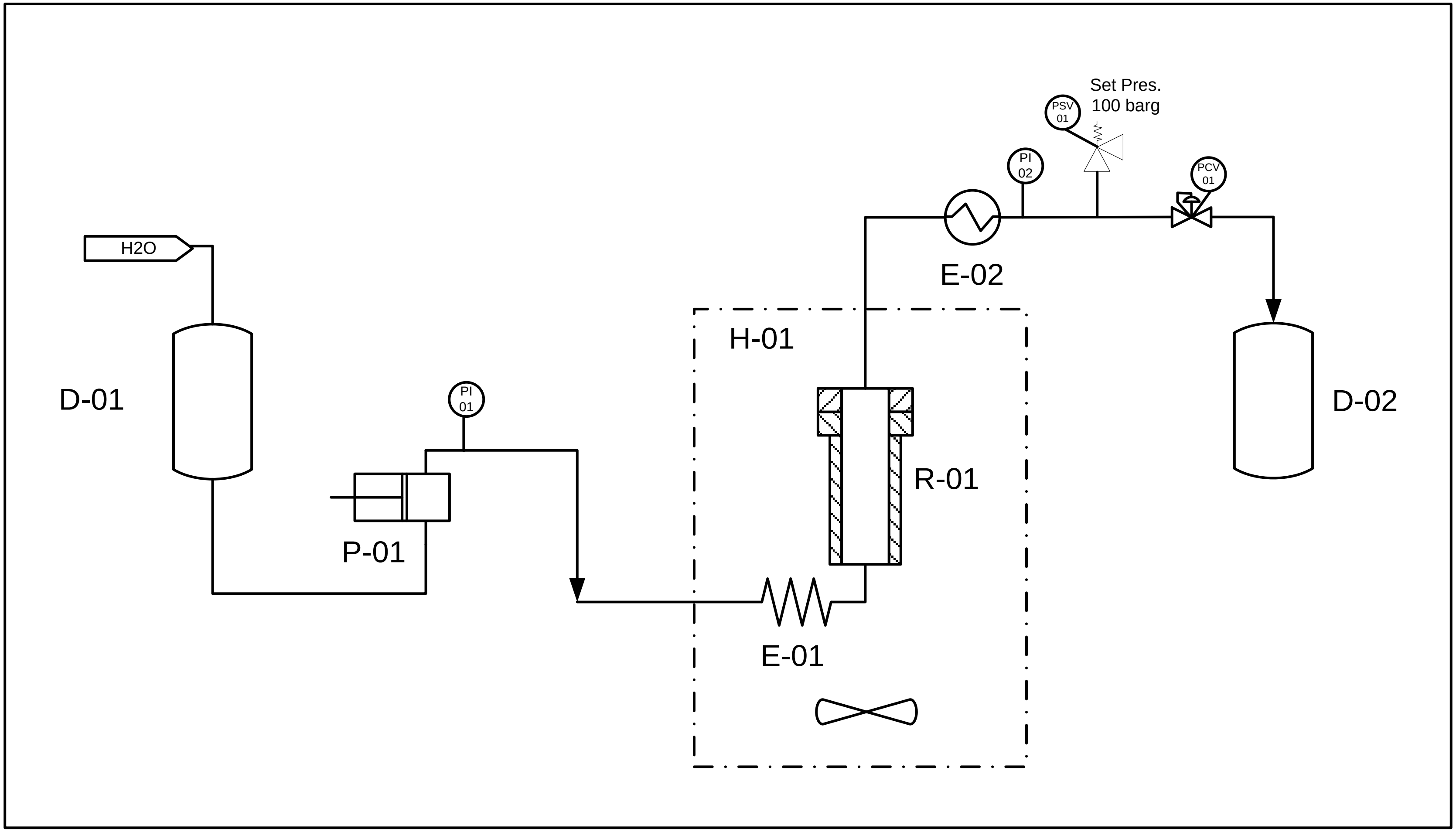
6 fractionation *via* hydrolysis

- Acid hydrolysis
- Enzymatic hydrolysis
- Dissolution and hydrolysis in ionic liquids
- Hydrothermal processes
- SCW *processes*

6 fractionation *via* hydrolysis

BATCH	**HOURS**
SEMI-CONTINUOUS	**MINUTES**
CONTINUOUS	**SECONDS**

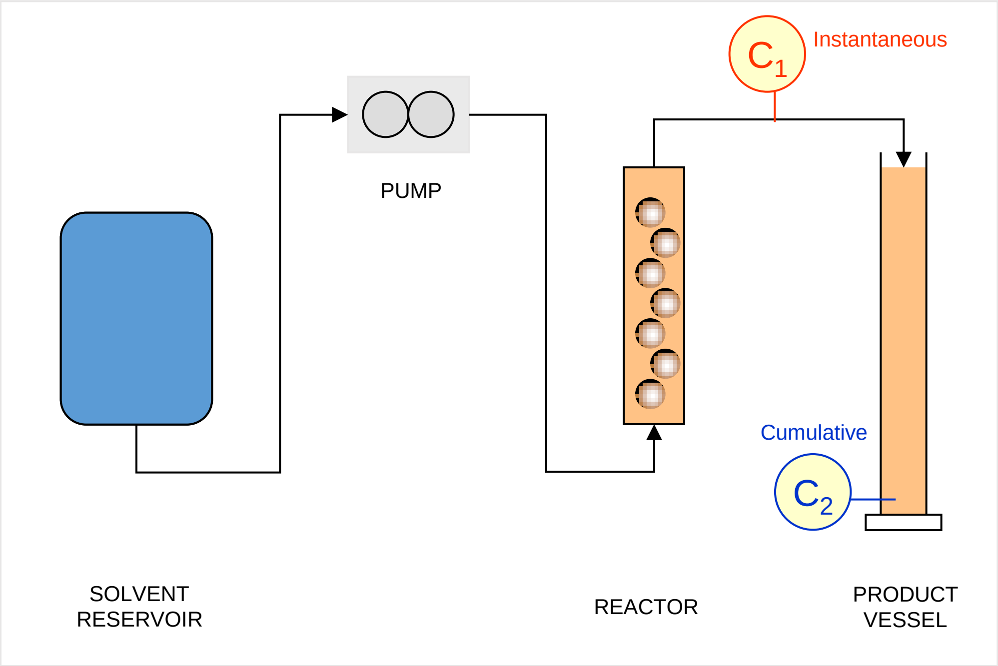
6 fractionation – semicontinuous

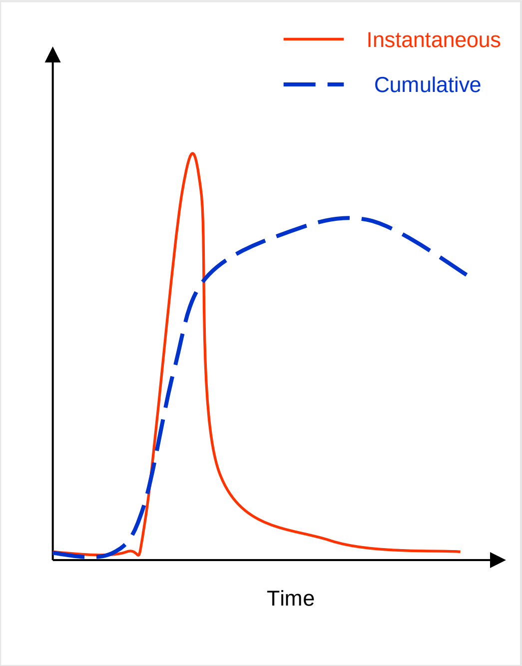


D-01	P-01	E-01	R-01	E-02	D-02
H_2O FEED VESSEL	***H_2O FEED PUMP***	***PREHEATER***	***EXTRACTOR-REACTOR***	***PRODUCT COOLER***	***PRODUCT VESSEL***

6 fractionation – semicontinuous

SOLVENT → CONTINUOUS **BIOMASS → BATCH**

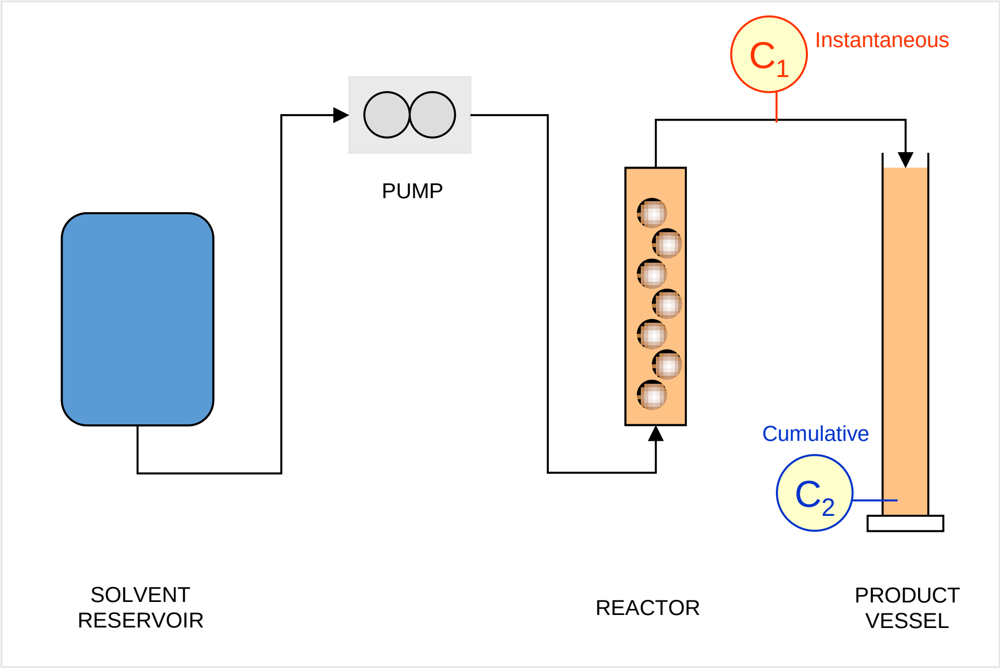


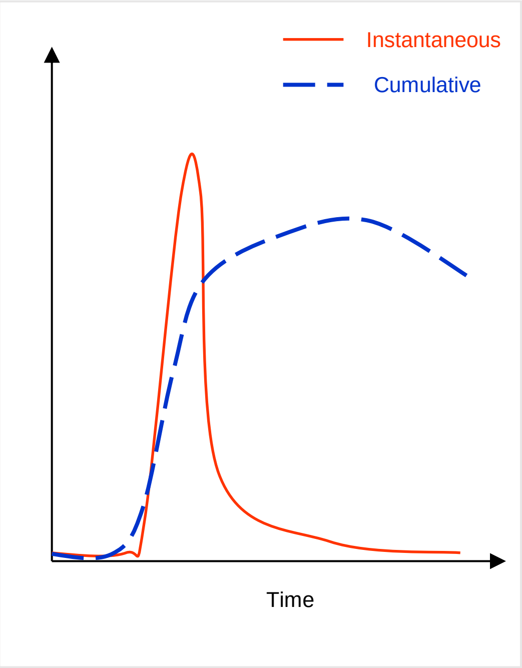


SEMICONTINUOS MODELLING → KINETICS OF THE PROCESS

6 fractionation – semicontinuous

SOLVENT → CONTINUOUS   BIOMASS → BATCH



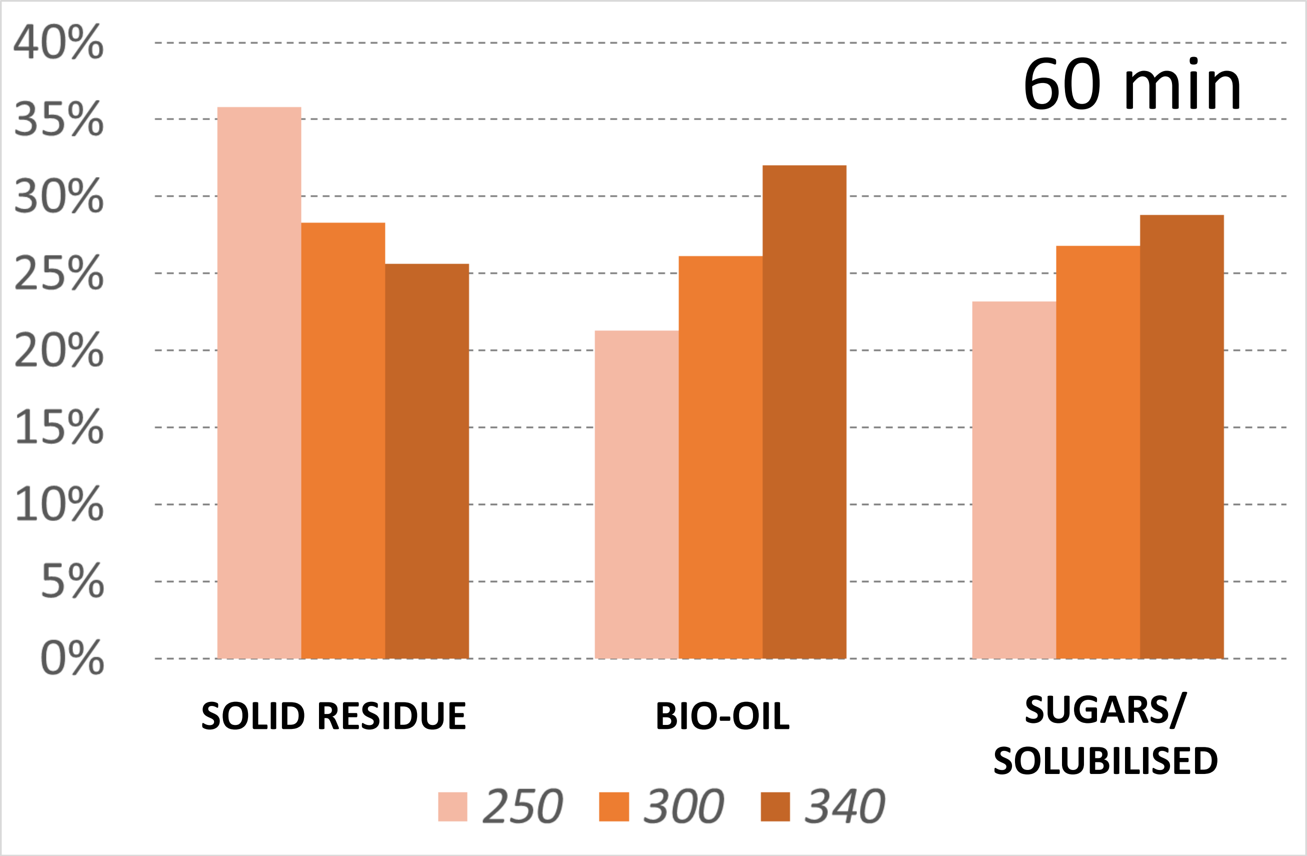


SEMICONTINUOS MODELLING → KINETICS OF THE PROCESS

H_2O only

H_2O + EtOH

EXPERIMENTAL PROCEDURE - SEMICONTINOUS

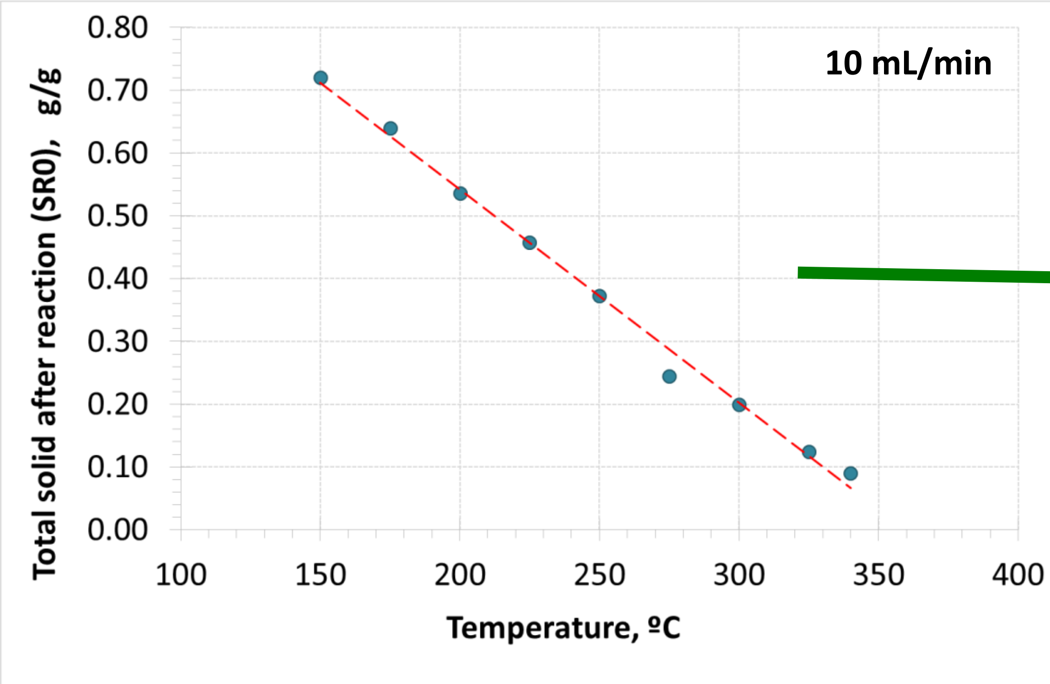


H_2O only

	SR	BO	SG	Mass Balance
250	36%	21%	23%	80%
300	28%	26%	27%	81%
340	26%	32%	29%	86%

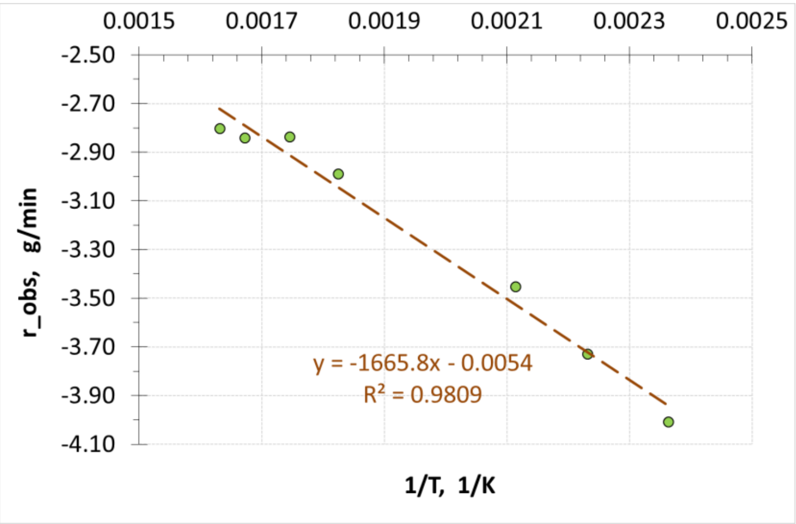
BIO-OIL PRODUCTION

H_2O only



E_a = 13850 J/mol

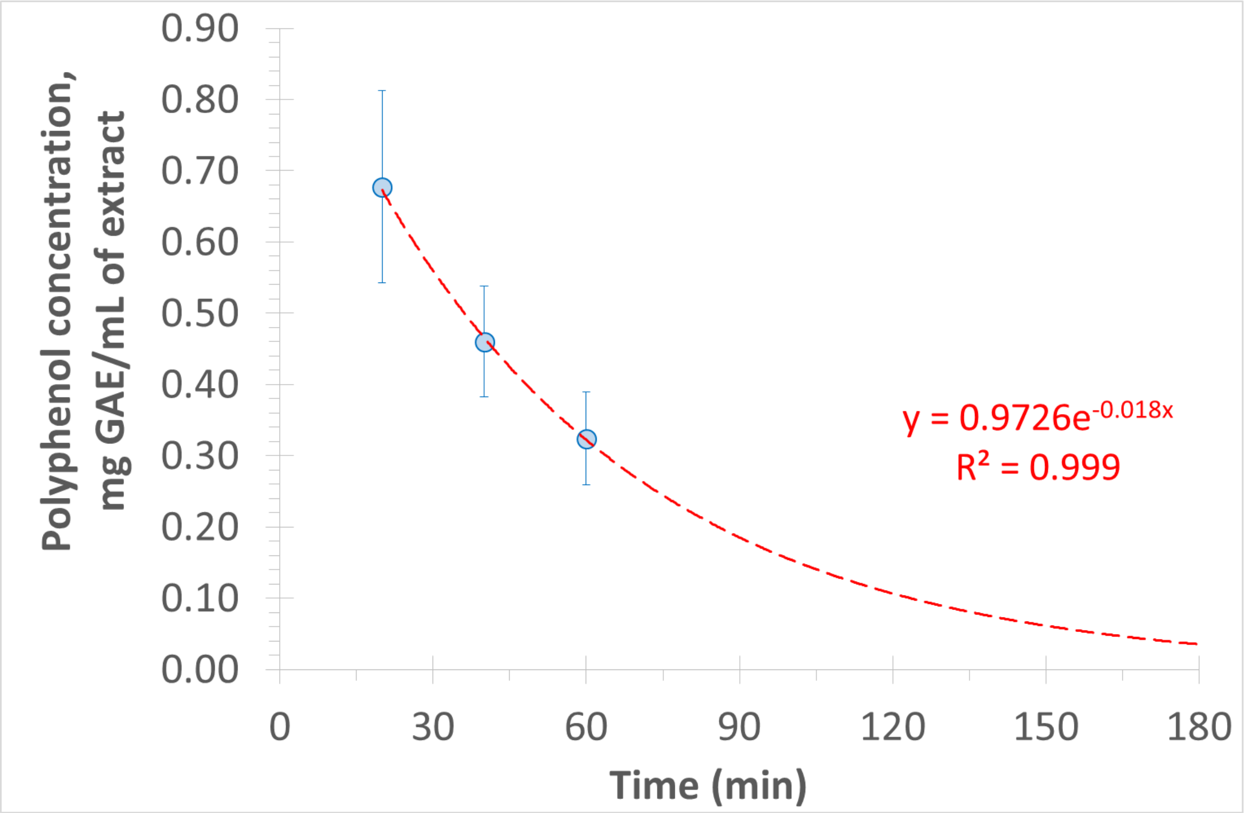
k_0 = 0.995 g/min

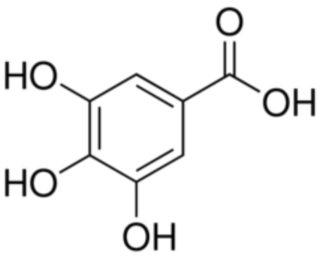


Only considering the solid with zero order can be explained, however mass is needed to explain the whole.

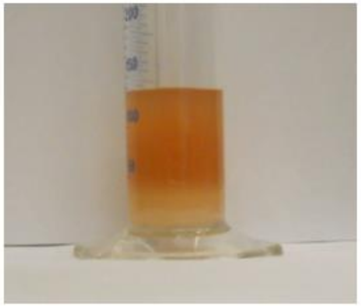
BIO-OIL PRODUCTION – SIMPLE KINETICS FOR SOLID

H_2O + EtOH

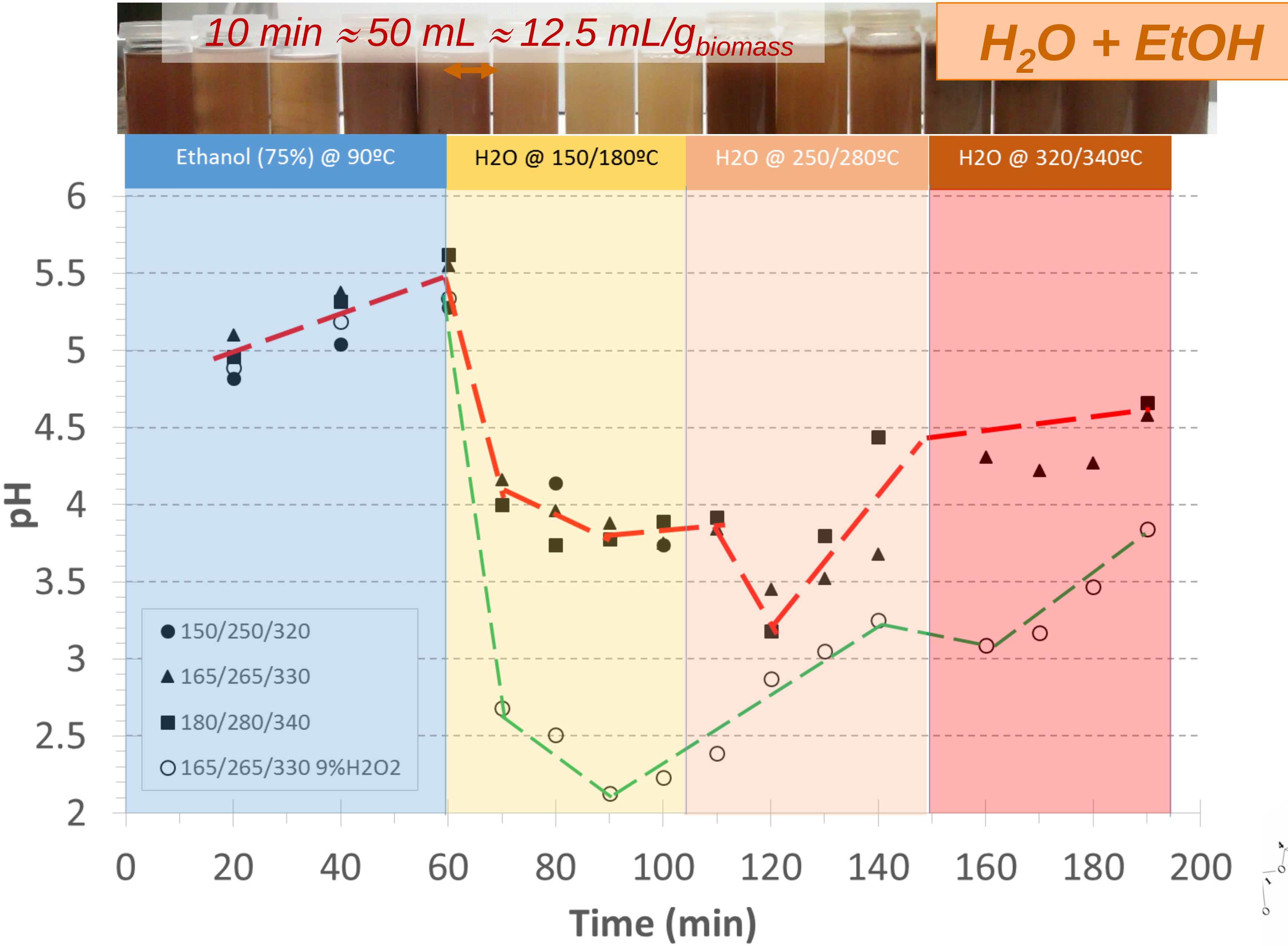




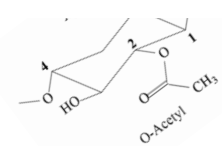
$$m_{GAE} = \int_0^t q \cdot c_{GAE_0} \cdot e^{-b \cdot t} = \frac{q \cdot c_{GAE_0}}{b}\left(1 - e^{-b \cdot t}\right)$$



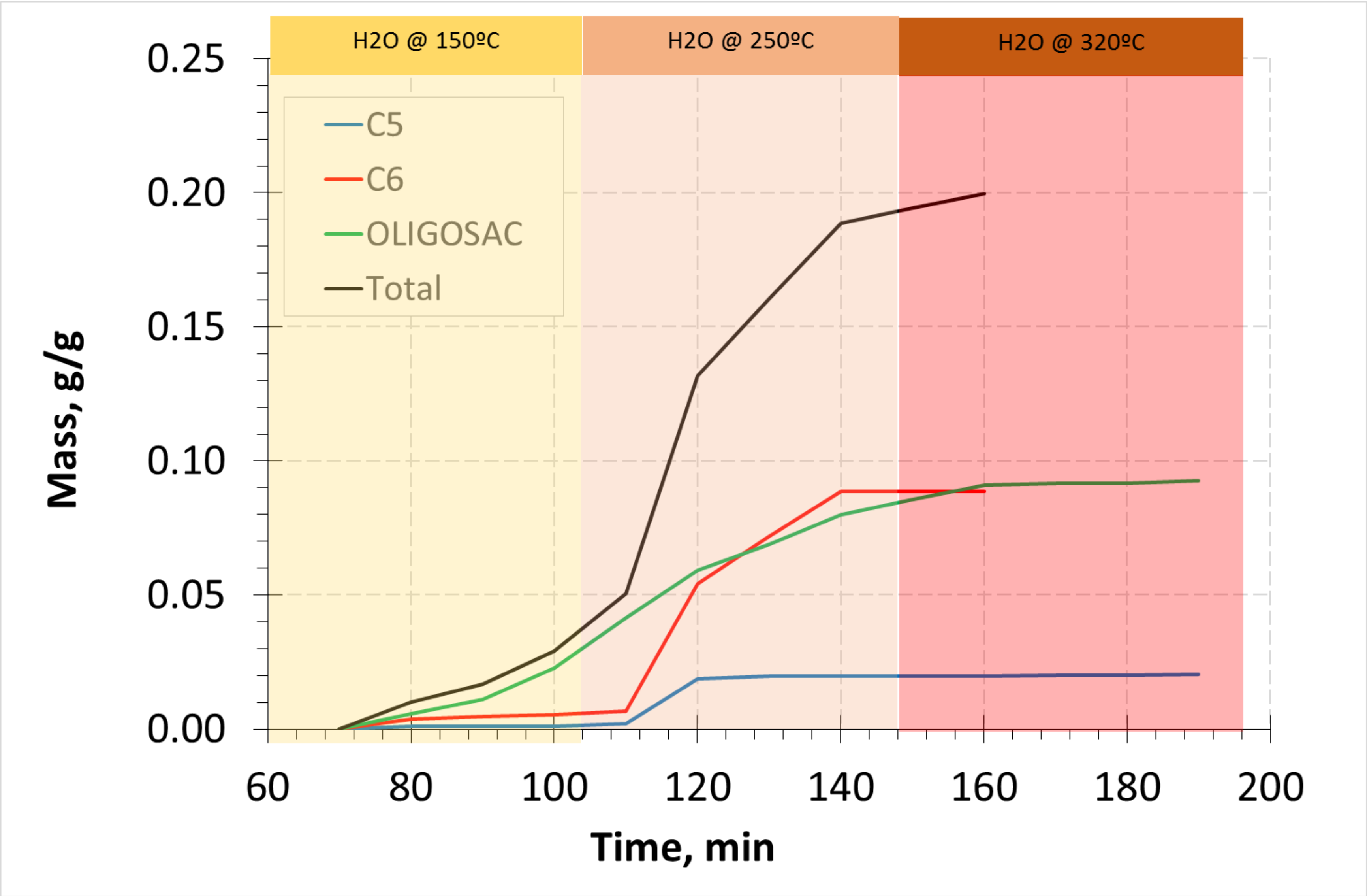
POLYPHENOL EXTRACTION



VARIATION OF pH AND ACETIC ACID FORMATION

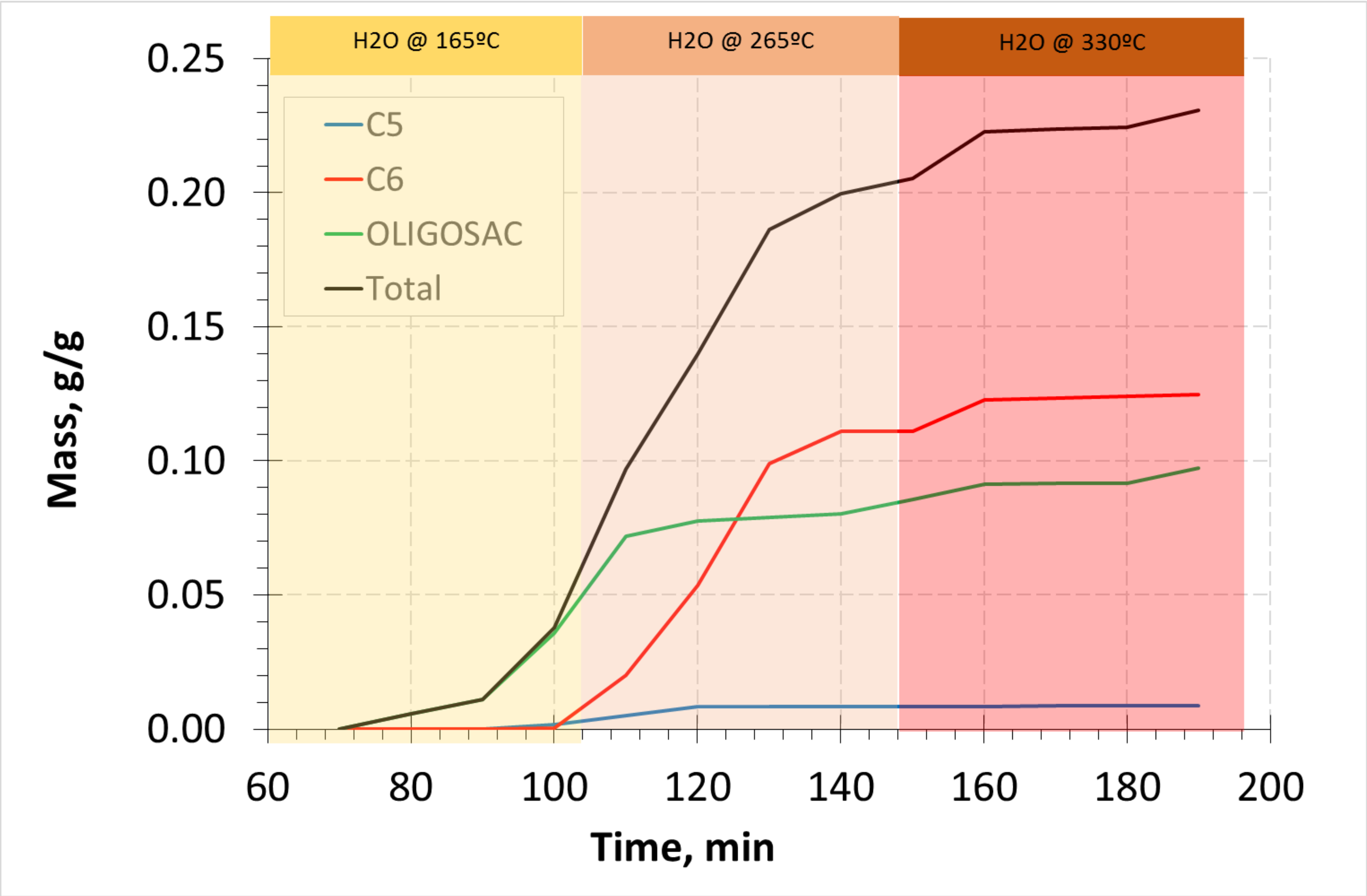


$H_2O + EtOH$



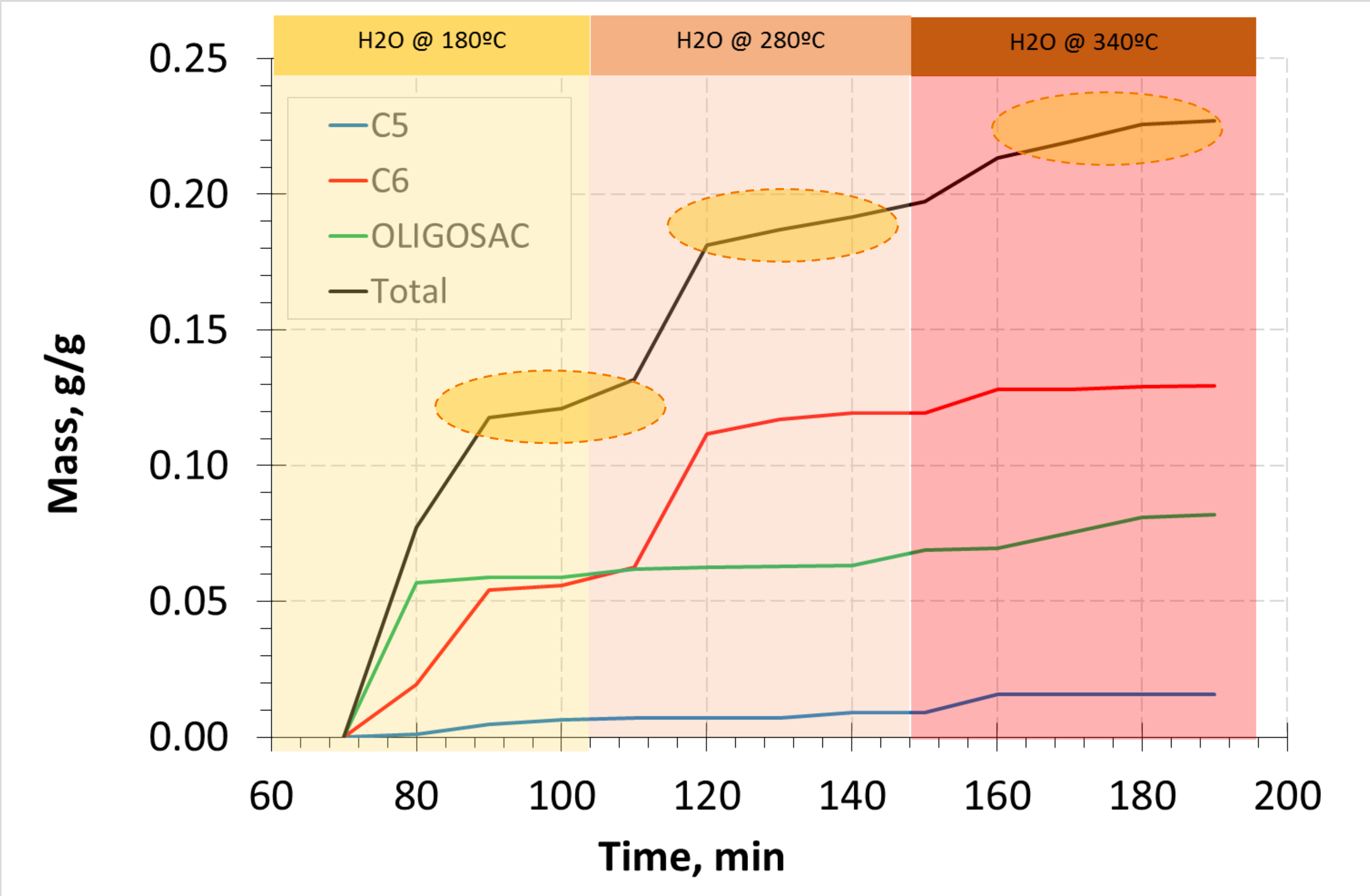
C5/C6 EXTRACTION + OLIGOMERS

H_2O + EtOH



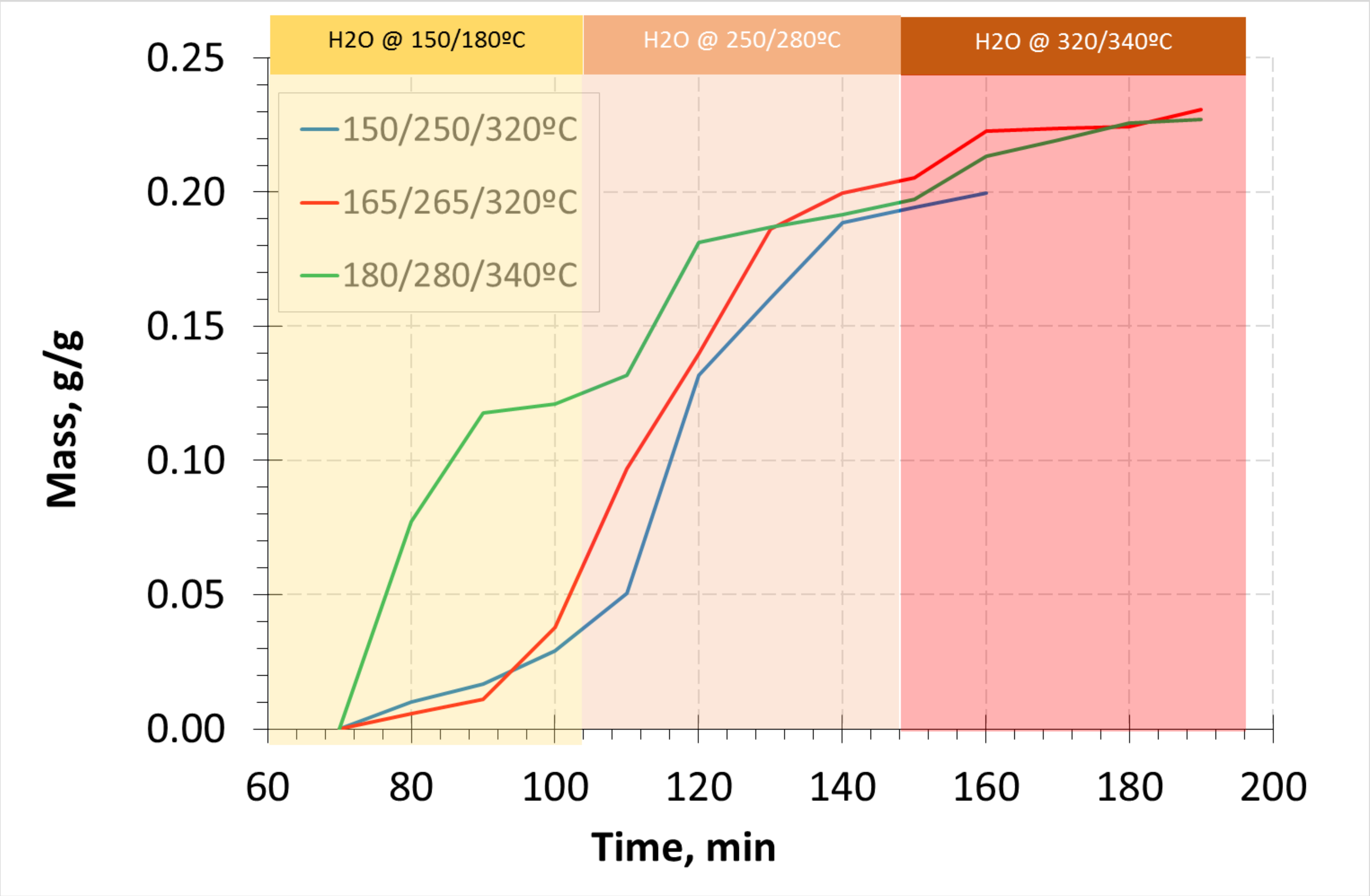
C5/C6 EXTRACTION + OLIGOMERS

$H_2O + EtOH$

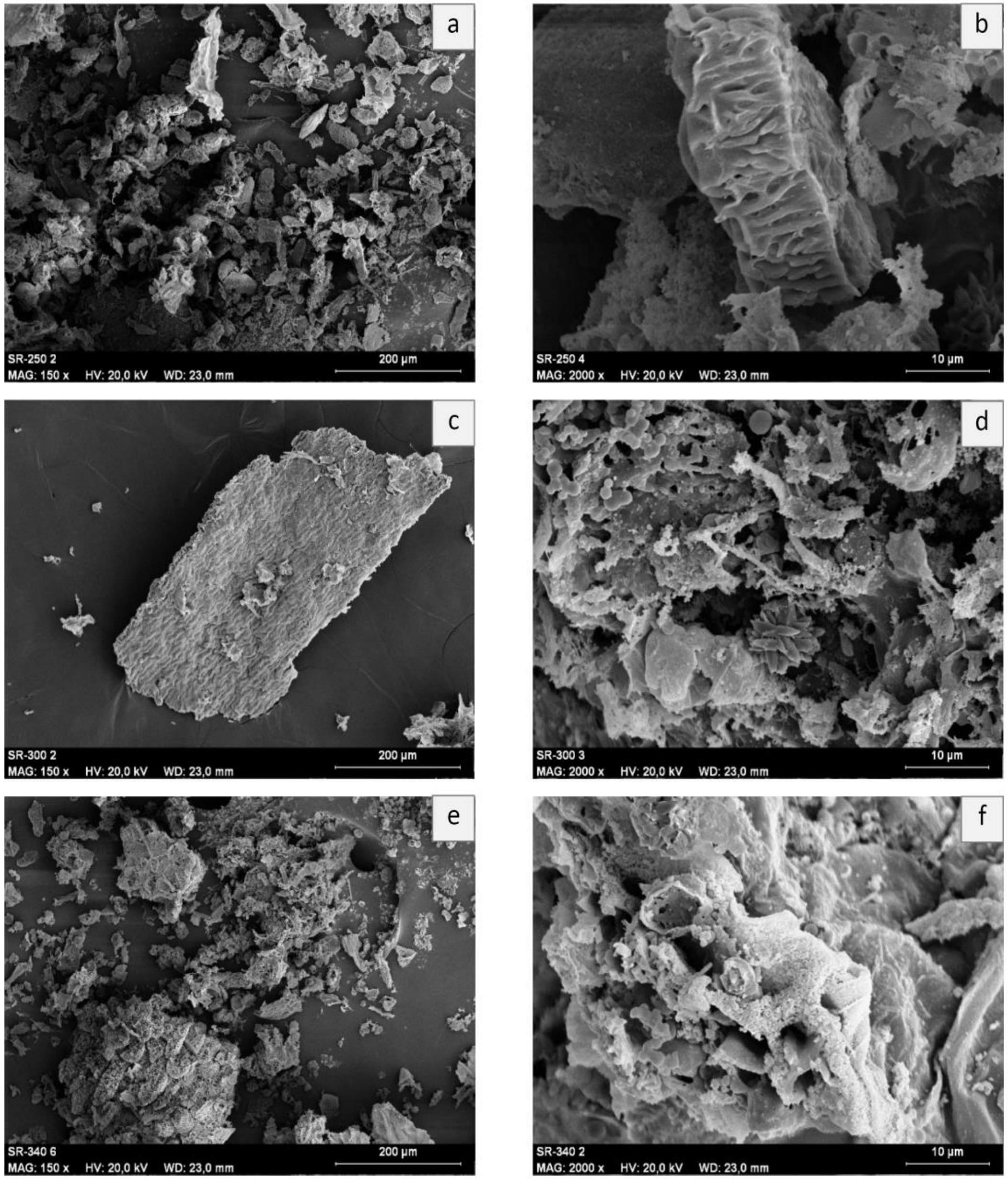


C5/C6 EXTRACTION + OLIGOMERS

H_2O + EtOH



C5/C6 EXTRACTION + OLIGOMERS



CARBONIZATION SEM

heat transfer

HEAT FLOW = ENTHALPY * FLOW

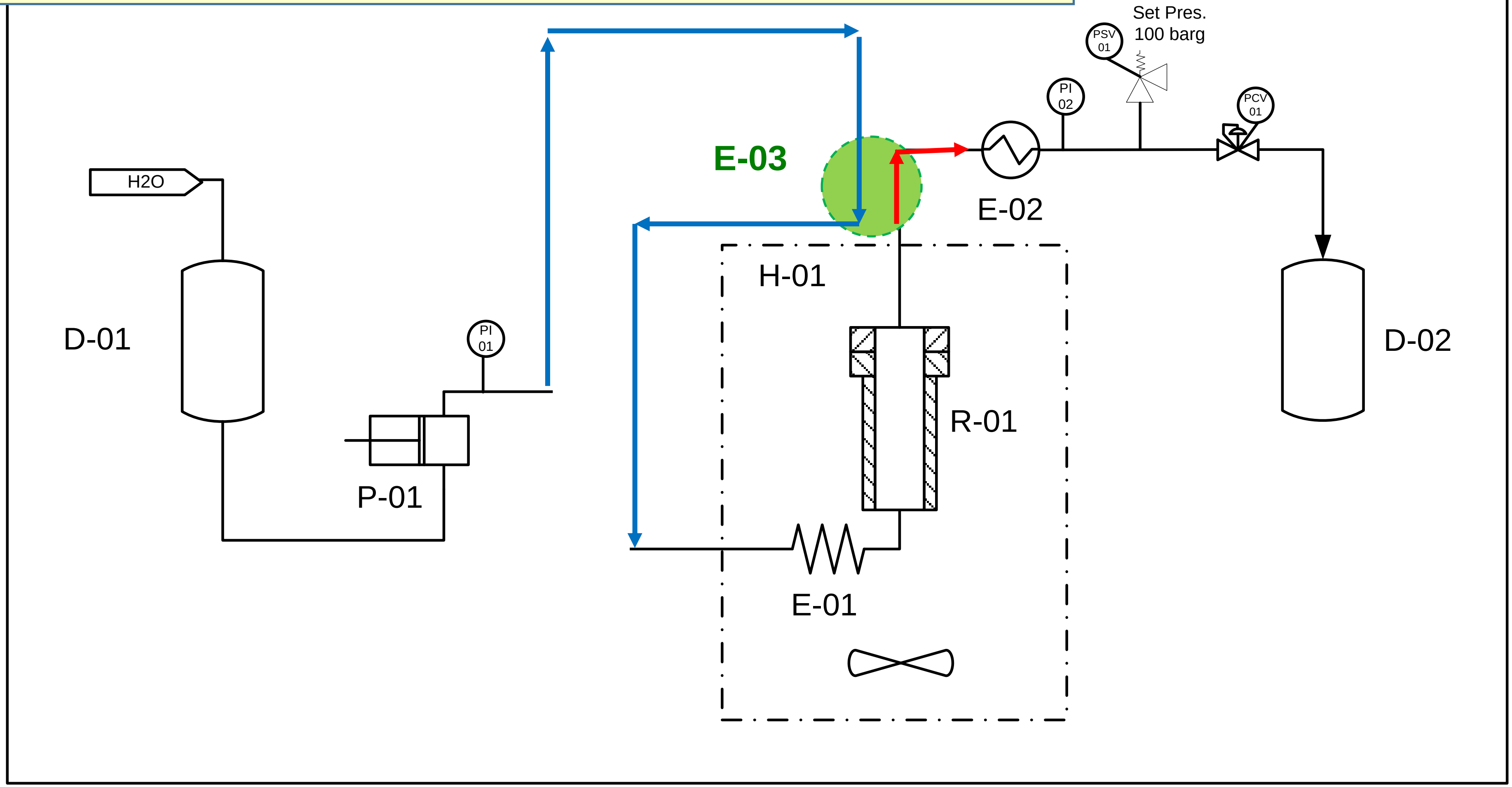
Liquid : $\Delta H = Cp \cdot \Delta T$

Vapor-supercritical: $\Delta H = Cp \cdot \Delta T + \Delta H_{vap}$

HEAT FLOW = U · S · ΔT

HEAT SAVINGS = 76% (high flowrate) to 82% (low flowrates)

COLD SAVINGS = 87% (high flowrate) to 98% (low flowrates)

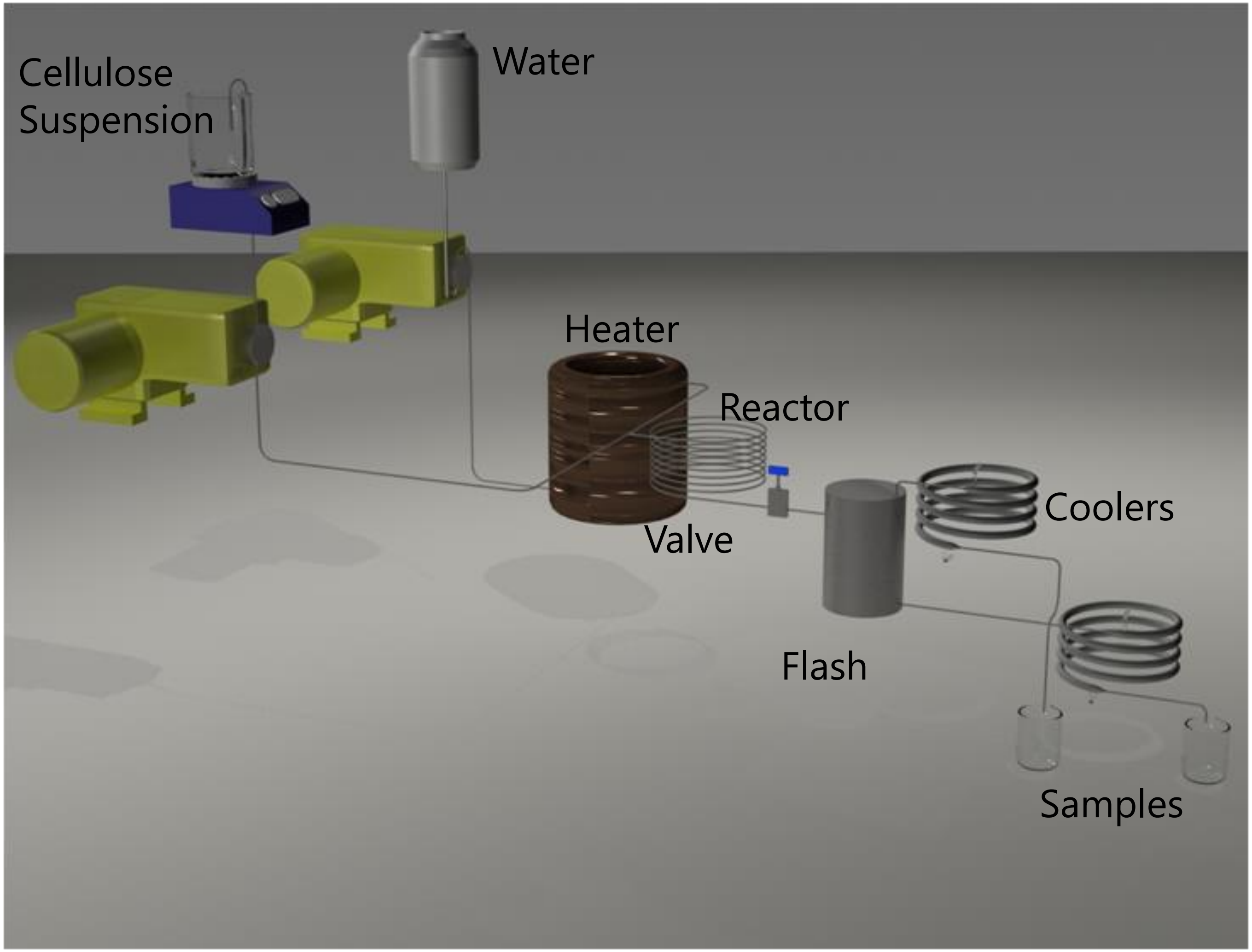


D-01	P-01	E-01	R-01	E-03	E-02	D-02
H_2O FEED VESSEL	***H_2O FEED PUMP***	***PREHEATER***	***EXTRACTOR-REACTOR***	***HEAT RECOVERY***	***PRODUCT COOLER***	***PRODUCT VESSEL***

HEAT INTEGRATION

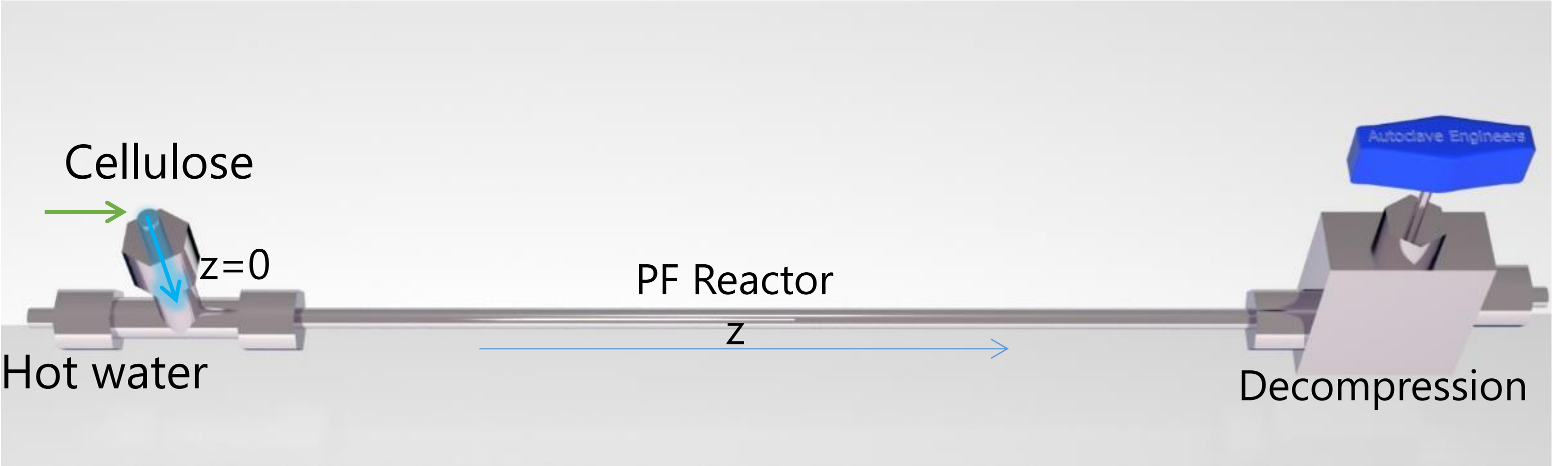
8 ultrafast - supercritical reation

Pressurization → Heating → Reaction → Cooling



Max T=400ºC
Max P=40 MPa
Long.= 0.03-6 M
Flow C= 1.5 kg/h
Conc. Cel. = 10 % w/w
Water flow= 10 kg/h
Res time = 0.004 – 40 s.

8 ultrafast - supercritical reation



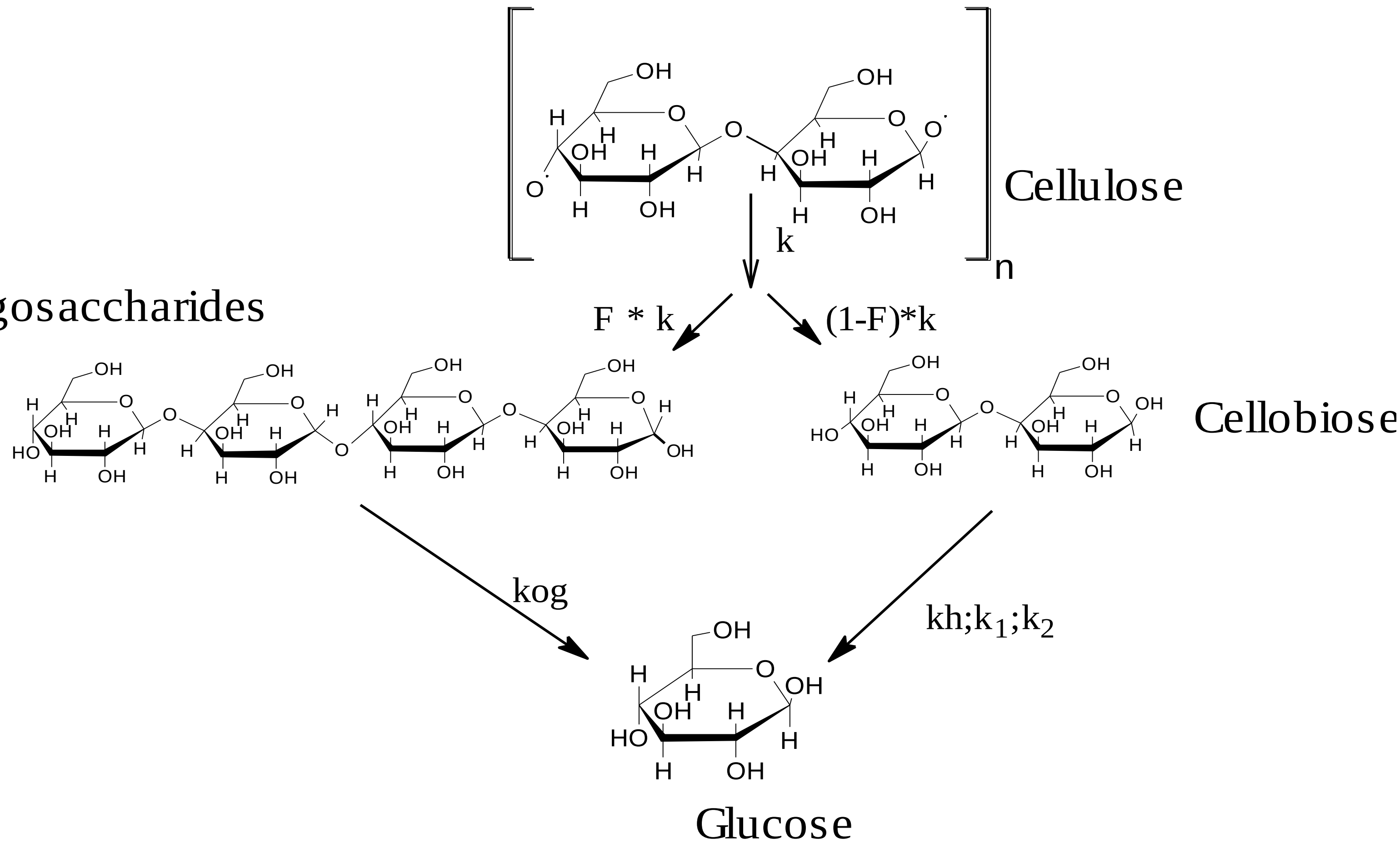
TRICK

HEAT QUICK

COOL QUICK

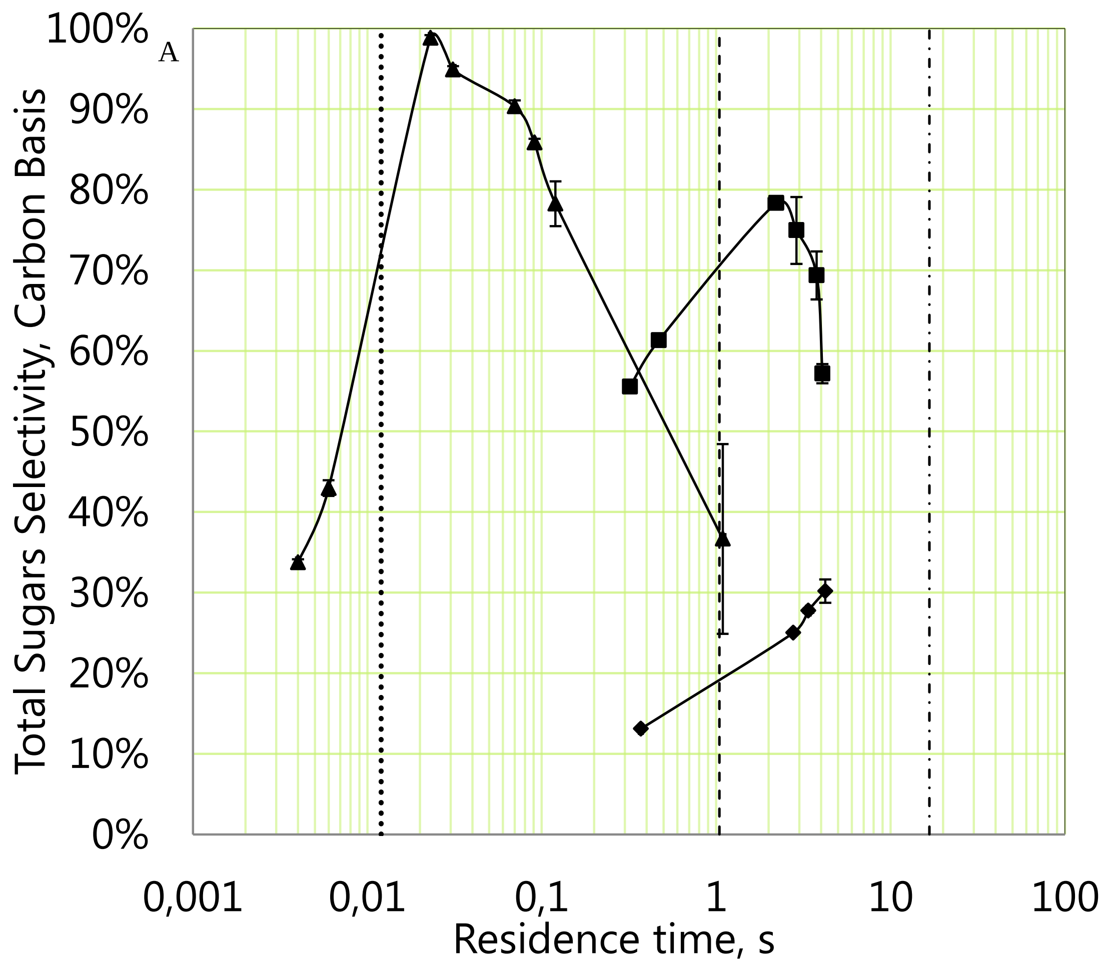
?

1st step of hydrolysis: oligosaccharides



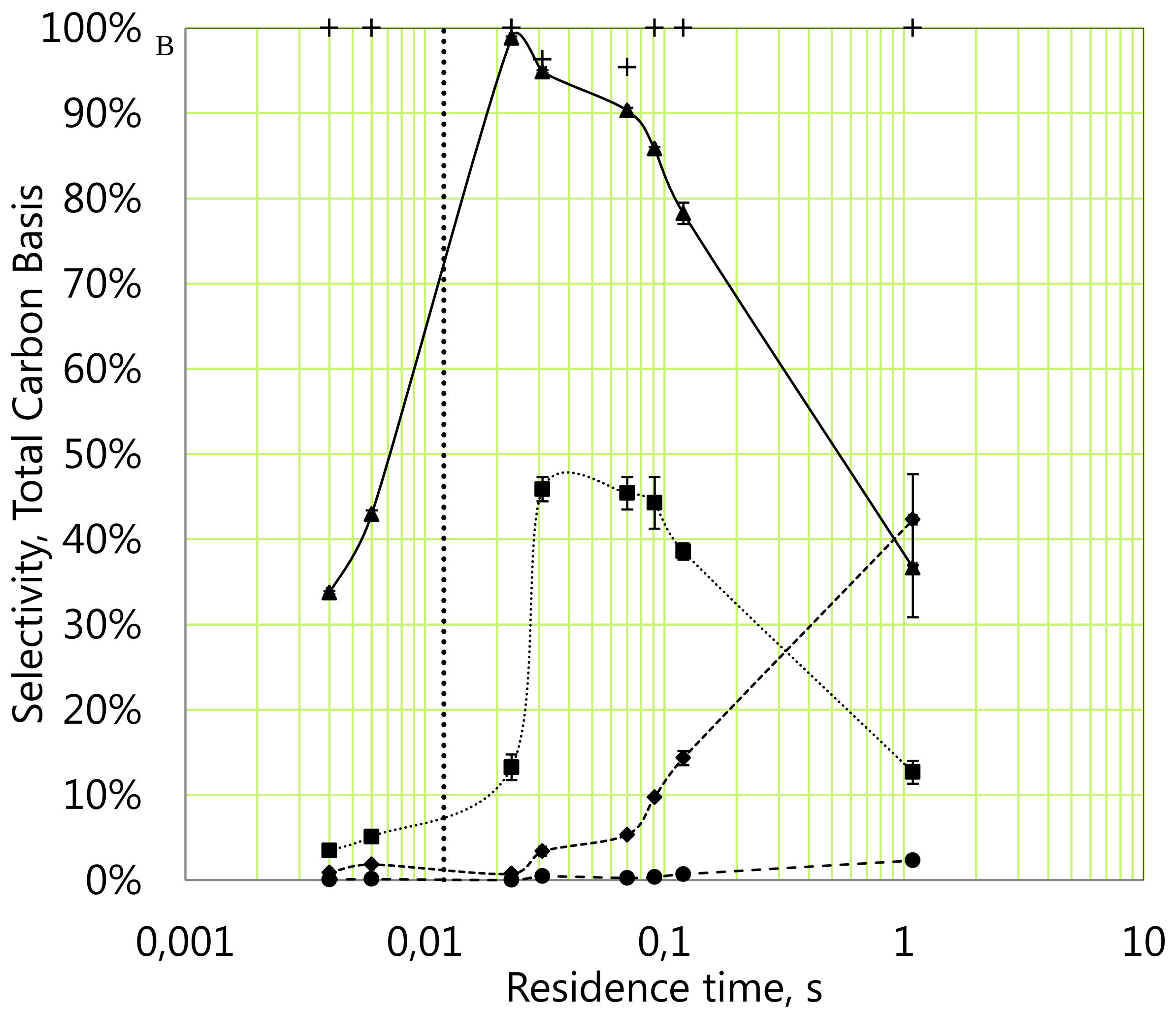
D Cantero; M D Bermejo; M J Cocero. Kinetic analysis of cellulose depolymerization reactions in near critical water. J Supercritical Fluids,. 75 - 48, pp. 48 - 57.. 2013.

Hydrolysis reactions selectivity



(♦) 300ºC, (■) 350ºC and (▲) 400ºC depending on residence time, dotted vertical lines are the residence times for total conversion at 300ºC, 350ºC and 400ºC respectively

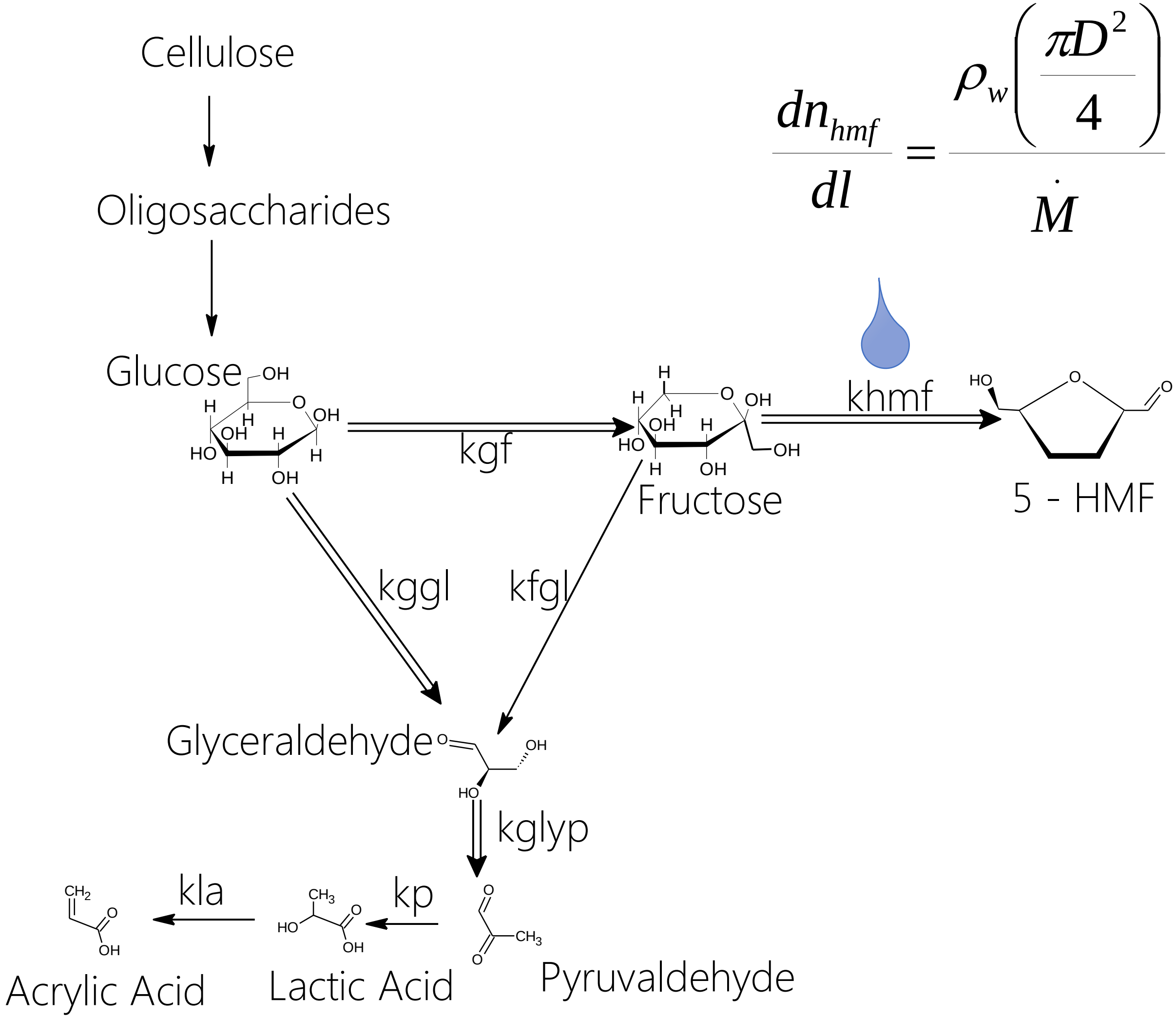
Hydrolysis reactions selectivity



Selectivity at 400ºC for: (▲) total soluble sugar, (■) glucose-fructose-cellobiose, (♦) pyruvaldehyde, (●)5-hydroxy methyl furfural, (+) Carbon Balance

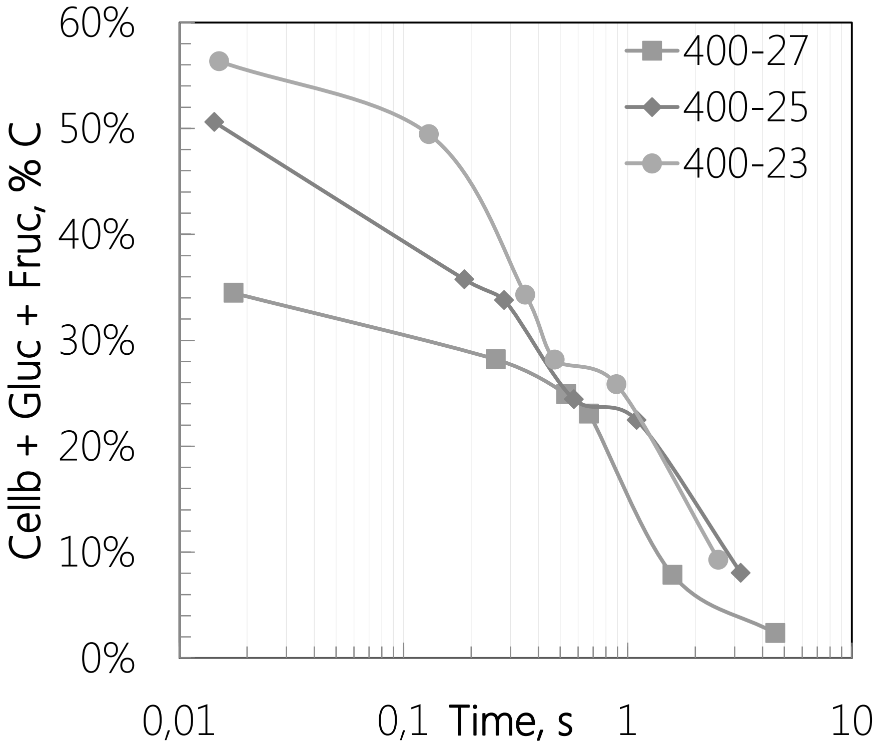
Reaction Pathway

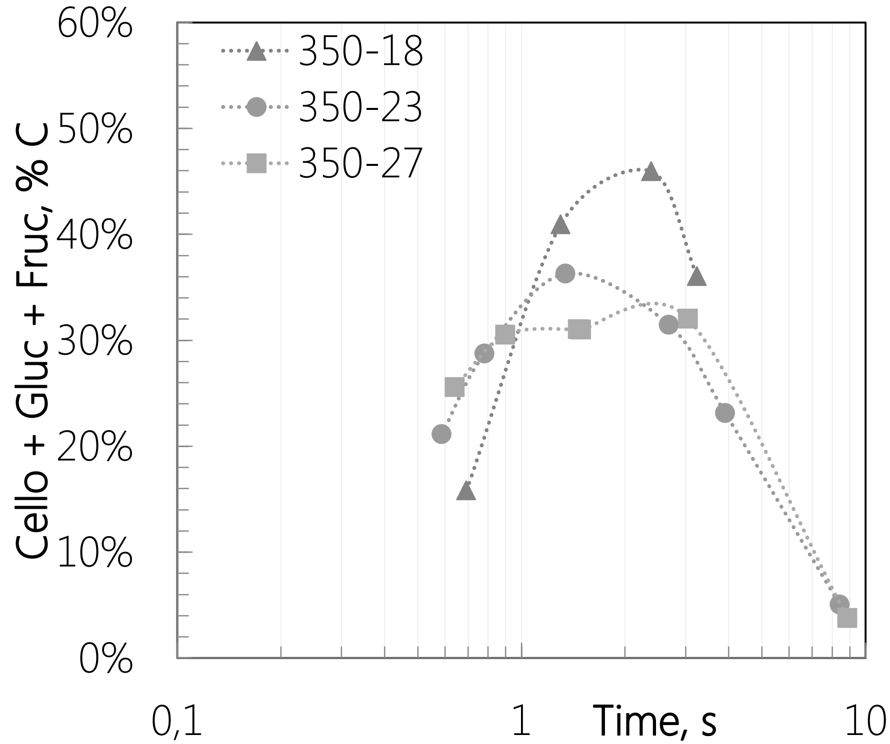
$$\frac{dn_{hmf}}{dl} = \frac{\rho_w\left(\frac{\pi D^2}{4}\right)}{\dot{M}}\left[k_{hmf} C_f C_w\right]$$



Kabyemela, B.M., et al., Industrial & Engineering Chemistry Research, 1997. 36(6): p. 2025-2030

Hydrolysis products: Sugars

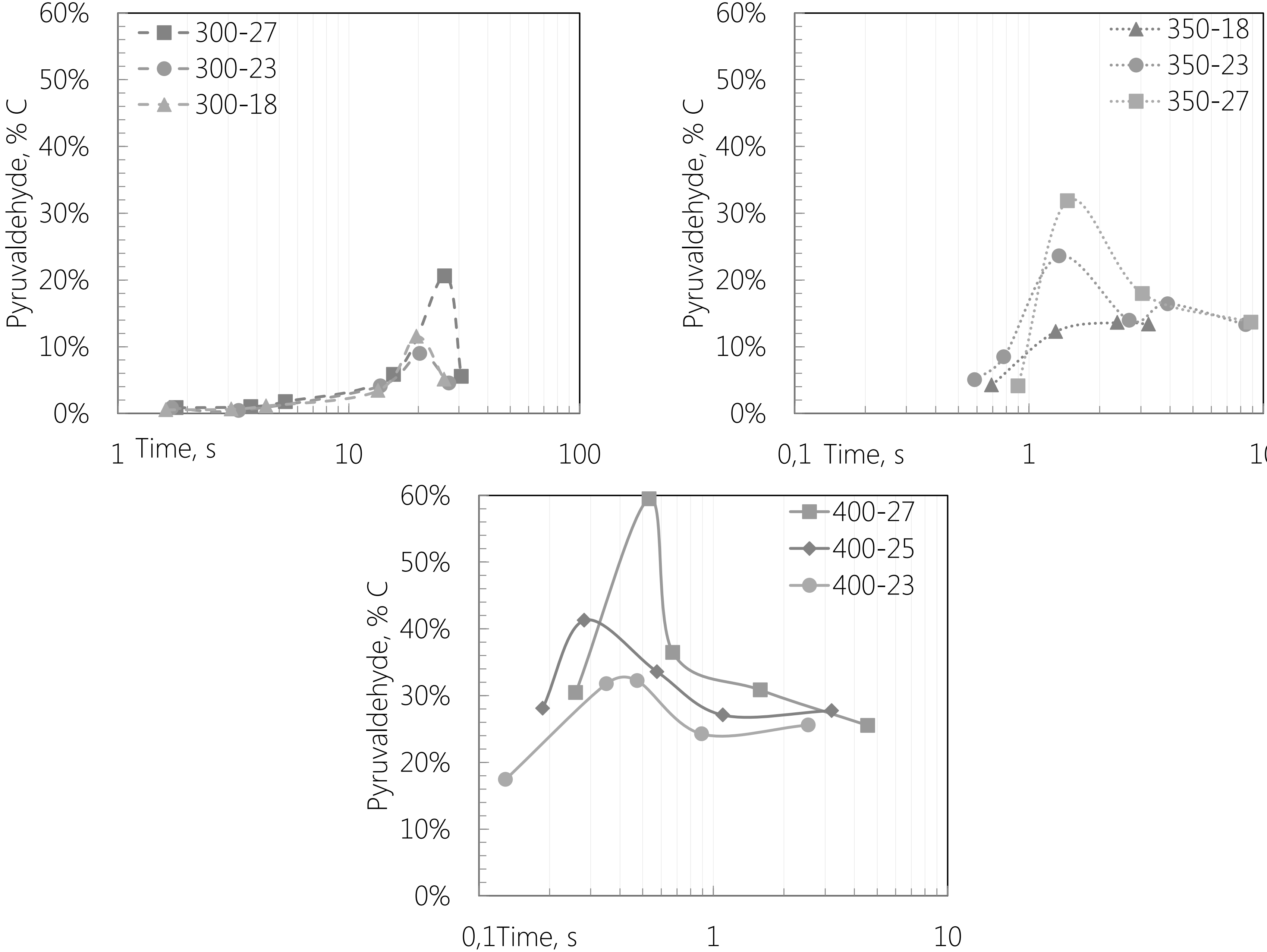




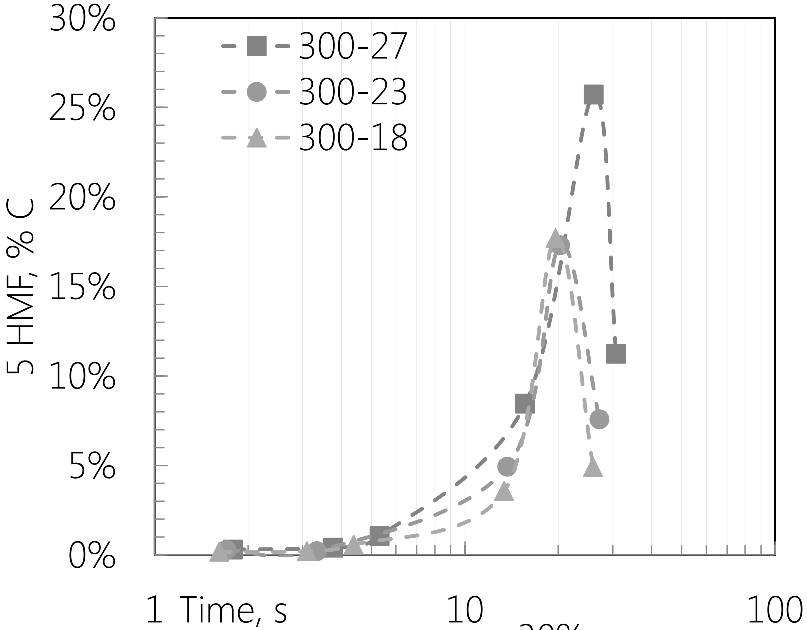
High selectivity at lower Pressure

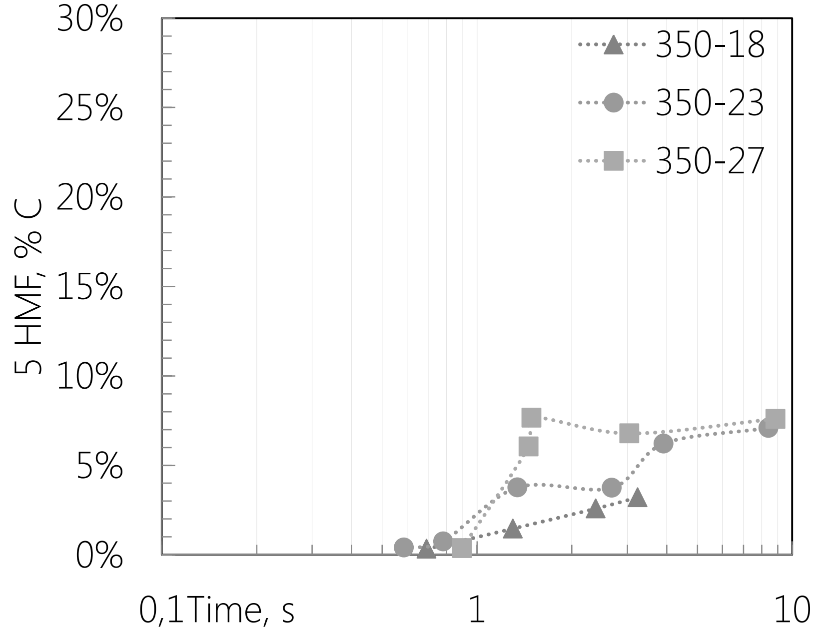
At 400ºC the selectivity reaches 98% if oligosaccharides are taken into account (cellotriose + cellotetraose + cellopentaose + cellohexose)

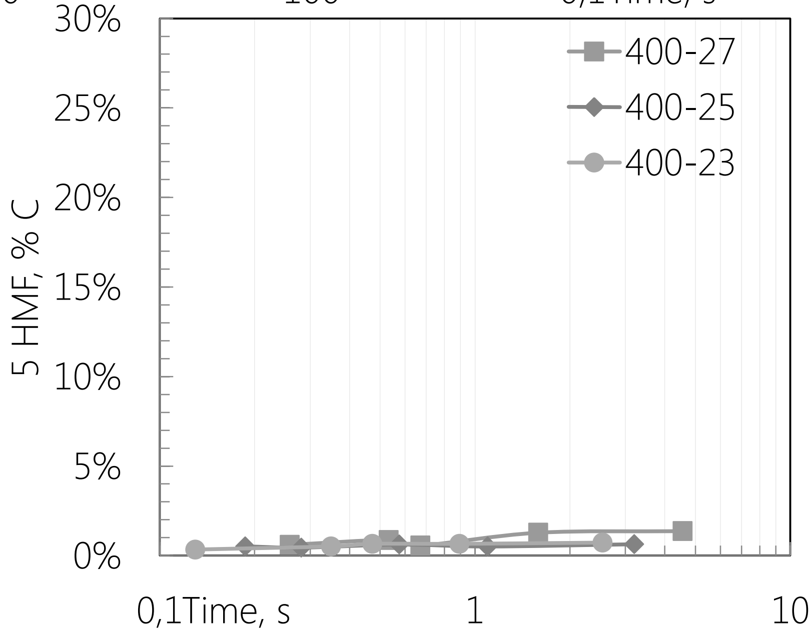
Hydrolysis products: Pyruvaldehyde



Hydrolysis products: 5-HMF







9 wheat bagasse separation

Reaction Conditions

Temperature: 327 – 387 ºC

Pressure: 30 MPa

Reaction Time: 0.35 – 0.5 s

High purity cellulose

Cellulose purity: 89.8- 100%

Initial Effluent

24 h

Effluent after 24h

Solid-Liquid separation

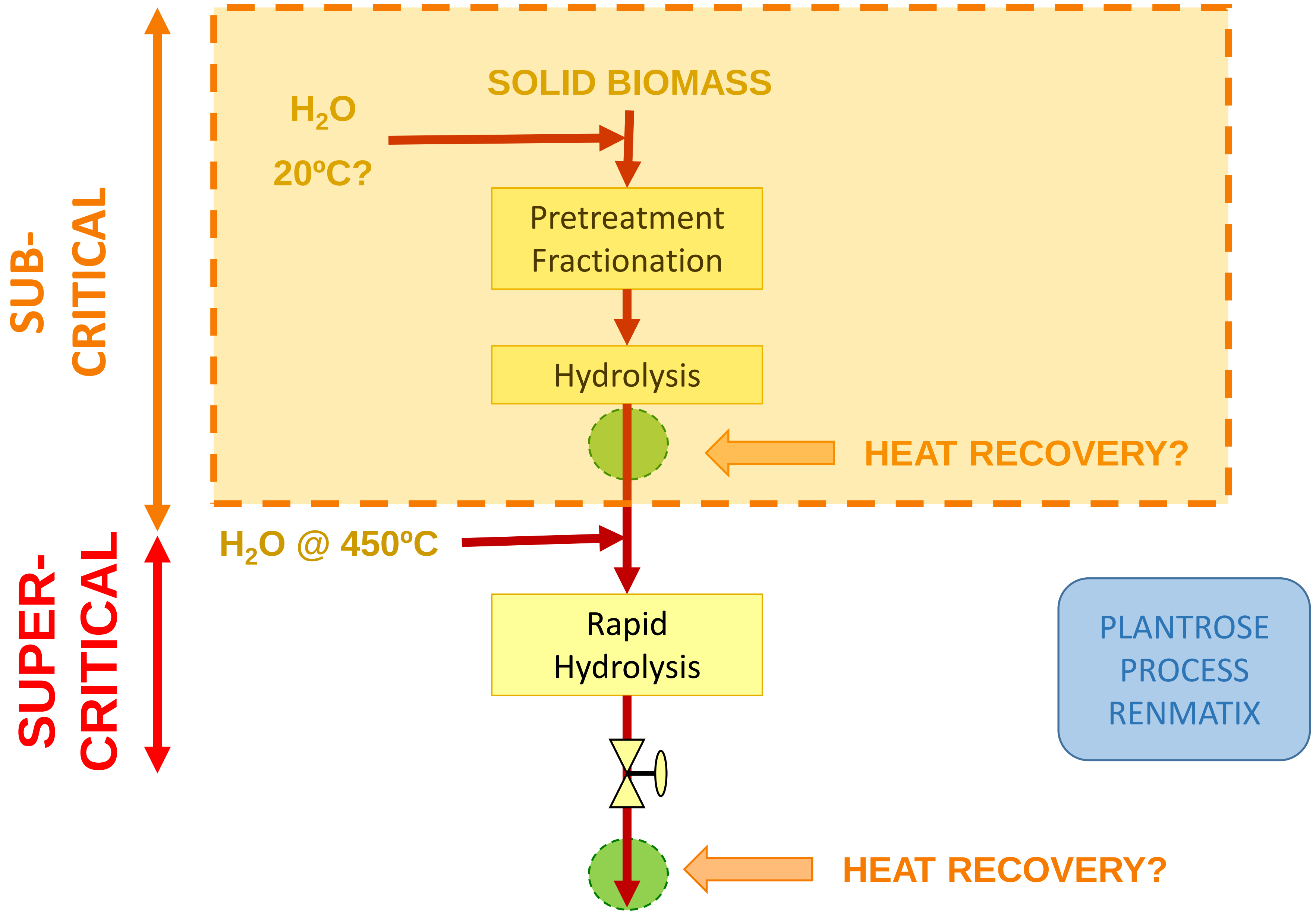
Cellulose solid

Separation of Cellulose from Lignin and Hemicellulose degradation liquid products

glucose conversion

Conditions			Selectivity		
P	Residence time (s)	Catalyst / Reagent	Pyruvaldehyde	Lactic Acid	Acrylic Acid
230	20.0 ±0.3	-	0.85	0	0.01
230	43.5±1.7	NaOH	0	0.08	0.03
270	12.1±0.1	H_2O_2	0.26	0	0.14
270	10.0±0.1	H_2O_2	0.2	0	0.01
270	10.2±0.1	H_2O_2	0.11	0	0.03
270	10.2±0.1	H_2O_2 + NaOH	0.09	0	0.02
270	40.1±0.5	H_2O_2 + NaOH	0	0.4	0.05
270	30.0±0.5	NaOH	0	0.05	0.01
270	33.2±0.5	H_2O_2 + NaOH	0	0.06	0.03

optional process

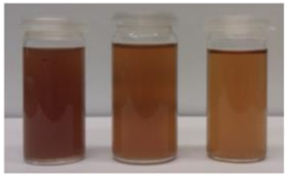


in a nutshell...

THE SWEET LIFE OF AN IDEAL GRAPE

1. Ethanol + H_2O

2. Subcritical H_2O



OIL+
POLYPHENOLS

LIGNIN PRODUCT

HYDROLYZED SUGARS

in a nutshell...

OILY LIFE OF A BIOHYDROTHERMALISED GRAPE SEED

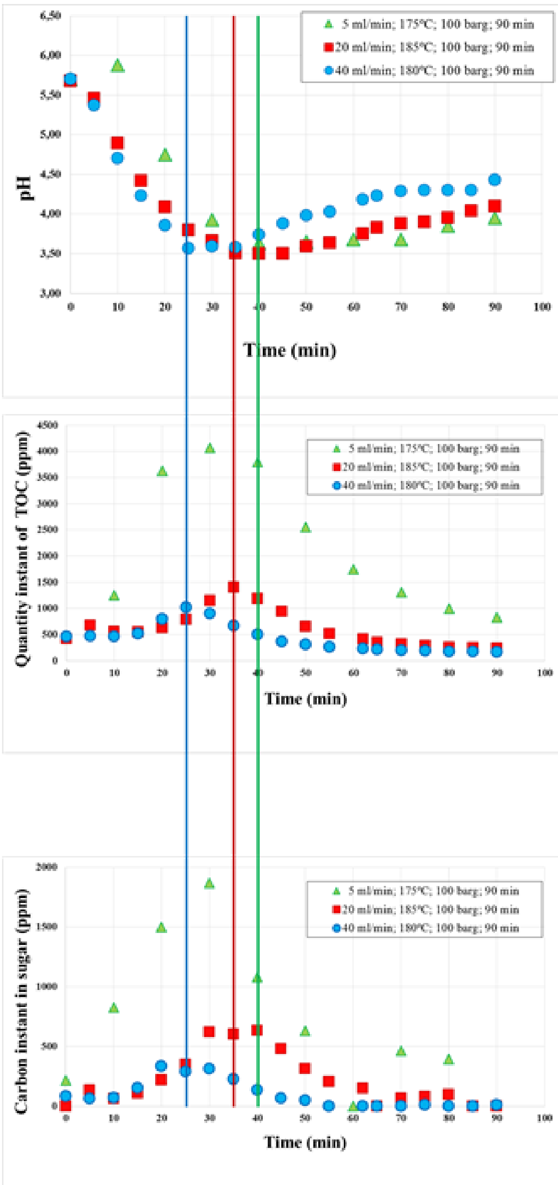
H_2O

SUBCRITICAL WATER

HEAVY & LIGHT BIO OIL

LIGNIN PRODUCT

in a nutshell…

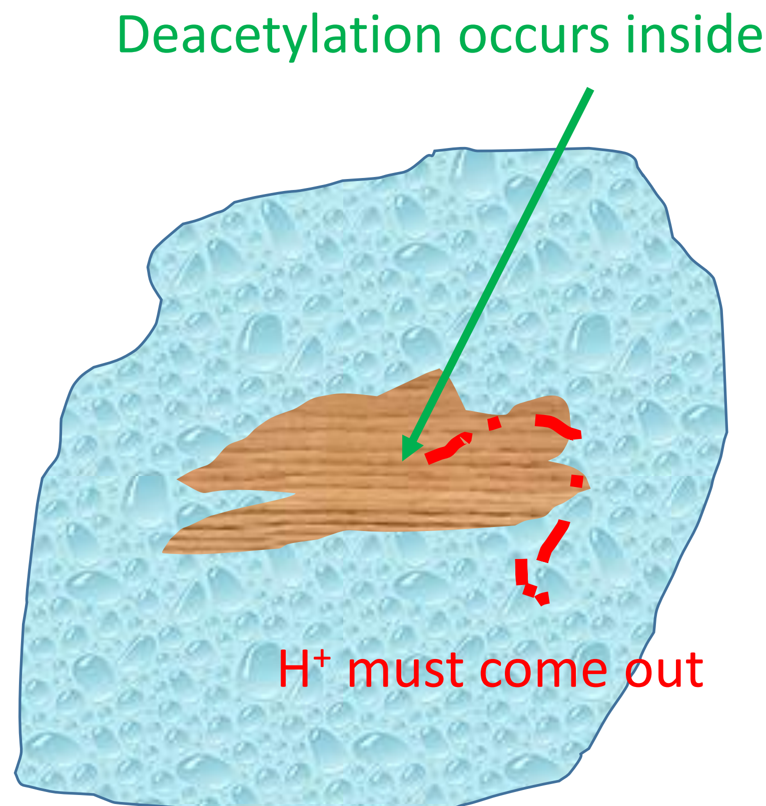


THE FORGOTTEN URBAN TREES BEING HAIRDRESSED

Cheap

Rapid

Precise



in a nutshell... on going

QUANTITATIVE SIMULATION OF THE TGA

MODELLING OF BIOMASS DEPOL. POPULATION BAL.

COMBINED PROCESS SUBCRITICAL + SUPERCRITICAL

EXTRACTION OF HEMICELLULOSES AT HIGH MOLECULAR WEIGTH FROM HOLM OAK

(at Åbo Akademi, Turku)


GRACIAS