Which Fractionation Process can Overcome Techno-Economic Hurdles of a Lignocellulosic Biorefinery?

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Outline

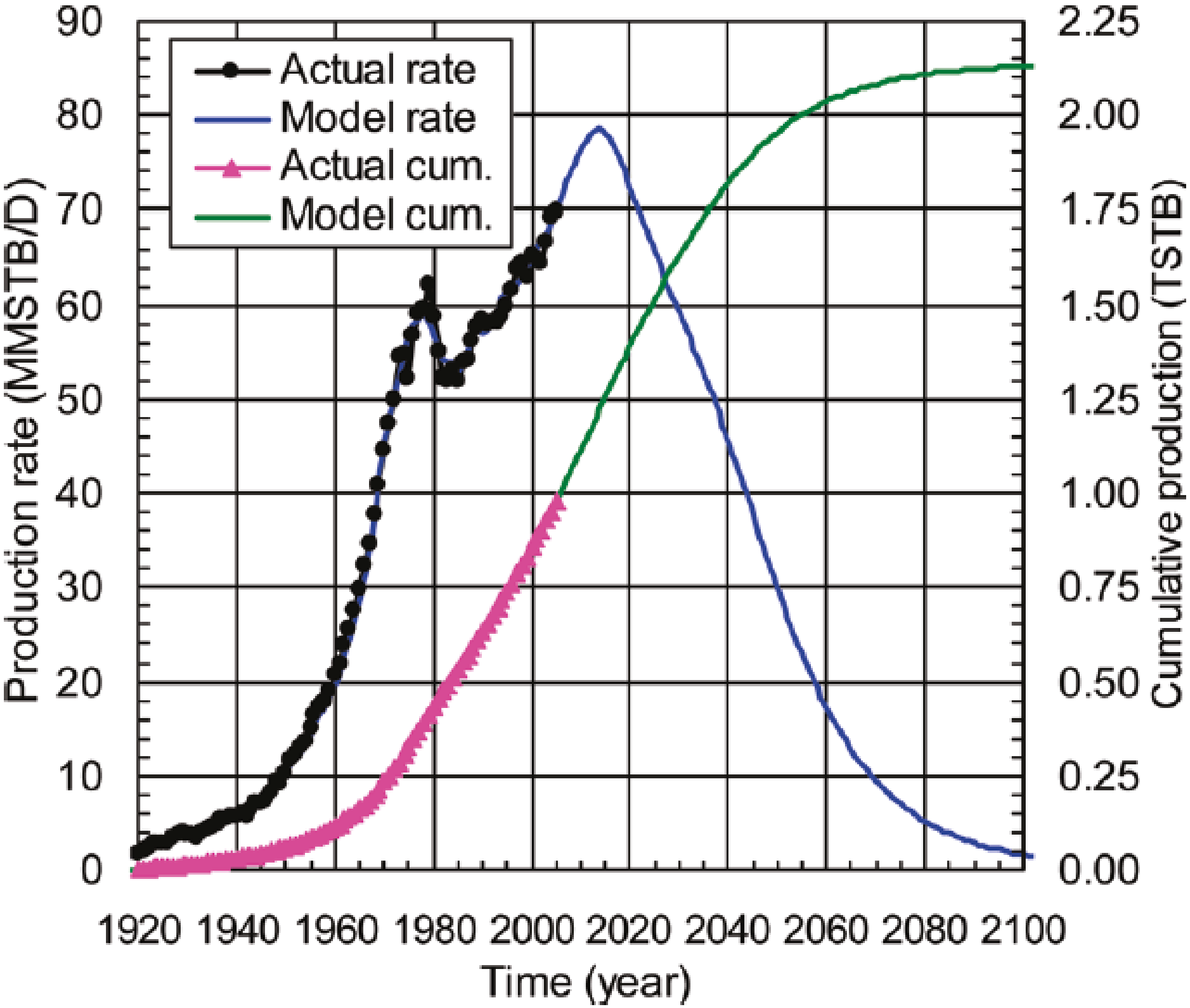
- Two most pressing global problems
- Two tech-econ. barriers for lignocellulosics
- Integrated forest biorefinery pathways
- AVAP® fractionation process
- Comparison of pretreatment/fractionation processes
- Conclusions

Two Most Pressing Global Problems

- Energy sustainability
- Climate change

how much time have left?

World Crude Oil Production Model



Multicyclic Hubbert model for 47 major oil countries

World peak-oil in 2014 at 79 MMSTB/D

Non-OPEC peak-oil in 2006 at 40 MMSTB/D

Presently ~50 % oil remaining

Nashawi, I. S. et al., Energy Fuels 2010, 24, 1788–1800

CO_2 Emissions and Global Warming

- CO_2 was 280 ppm in pre-industrial times
- Presently (2010) it is 390 ppm.
- Over 100 countries target global temp. rise to 2°C. This requires stabilization at 400 ppm CO_2
- Requires <1 trillion ton CO_2 emitted from 2000 to 2050.
- Today 1/3 of this has already been emitted since 2000

Meinshausen et al. "Greenhouse-gas emission targets for limiting global warming to 2 °C", ***Nature*****, 2009; 458, 1158-1162**

Opportunities and Challenges for lignocellulosic biomass

- Biomass is only sustainable source for production of liquid fuels and chemicals.
- Biomass is cheap at $12-24/BOE or €2-4/GJ.
- However there are **two** significant techno-economic barriers for lignocellulosics:
  - **Economy of scale is small compared to oil refinery because transport cost are high ($0.10/km/tonne)**

    → 2 MM DMT/Y wood vs 20 MM T/Y oil with LHV of 12 GJ/DMT vs 36 GJ/MT for fresh wood vs oil
  - **Cost effective fractionation and conversion technologies are not yet available**

Capital Cost Disadvantage due to Transport

- Petrochemical refinery: 20 GW
- Pulp mill (2 million dry ton wood): 0.7 GW

$$\frac{\left(\dfrac{\text{capital.cost}}{\text{ton fuel product}}\right)_{biorefinery}}{\left(\dfrac{\text{capital.cost}}{\text{ton fuel product}}\right)_{petrorefinery}} = \left(\frac{20}{0.7}\right)^{0.3} = 3$$

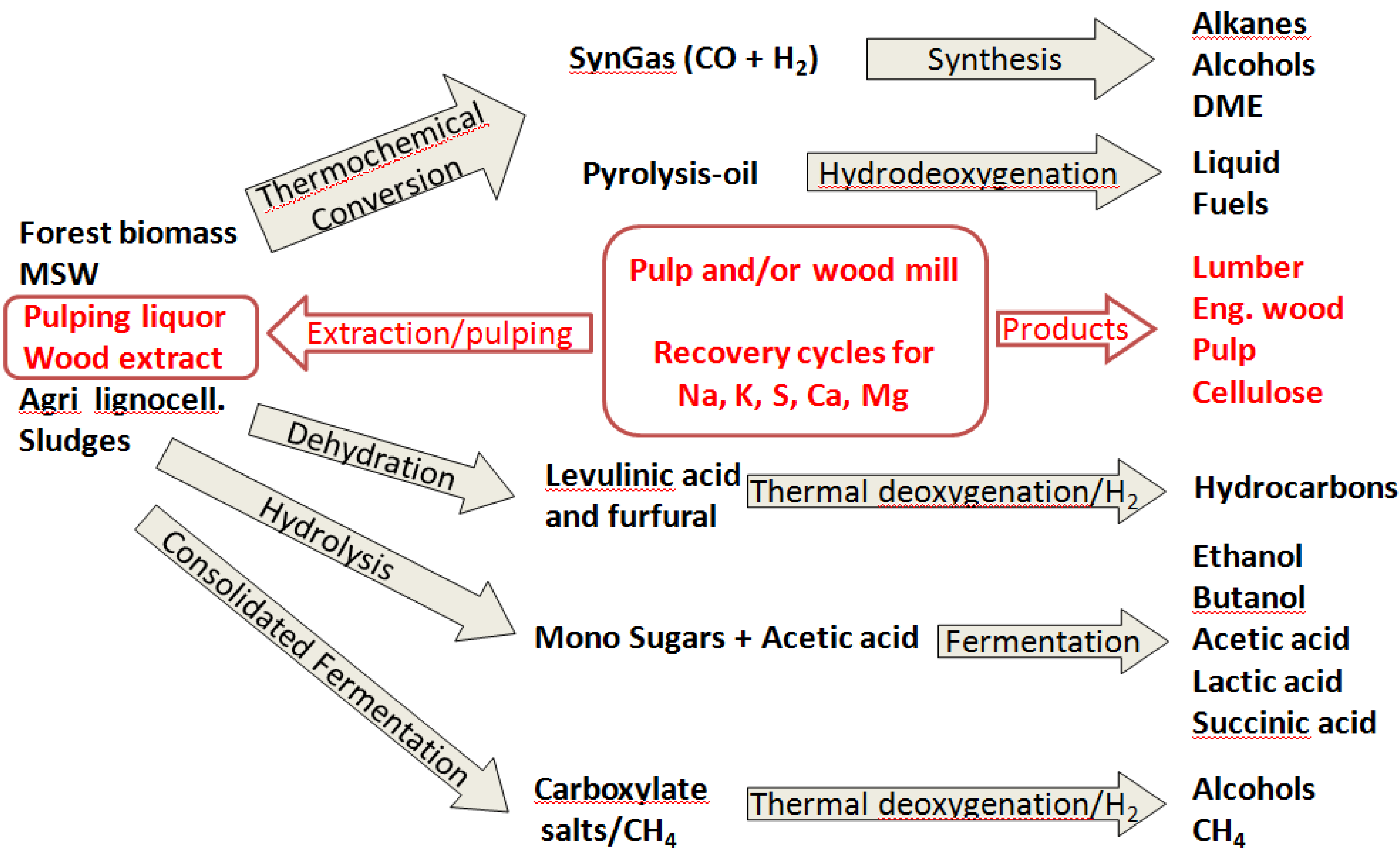
Capital Cost Disadvantage due to Technology

Industry	**Pulp**	**Petrochemical**
Principal continuous reactor	Digester	Cat cracker
Units in world	350	-
Throughput (tonne/day)	4000	3,000
Height (m)	45	40
Diameter (m)	10.5	1
Volume (m^3)	4000	30
Residence time (s)	10000	3
Space utilization ($kg/m^3.s$)	**0.01**	**1**

Pulp Mill as Biorefinery Site

- Saves 1/3 of infrastructure capital (vs. Greenfield)
  - Steam and power, water and effluent stations, warehouses, wood yards, storage tanks, etc.
- Already has operating permits
- Expertise in cellulosics procurement and logistics
- Modern kraft mill produces 30% excess energy.
- Produces base chemicals on-site (NaOH, CaO, etc.)

Integrated Forest Biorefinery Pathways



Ideal Fractionation Process

- Minimal feedstock requirements, i.e.
  - Omnivorous (annual fibers, hard- and softwood)
  - Able to fractionate commercial wood chips
  - Insensitive to moisture content
- All components (cellulose, hemicell. and lignin) available for products at high yields
- Produces hemi monosugars at high yield without enzymes at >100g/L
- Low charge of cellulose hydrolysis enzymes
- Simple + full recovery of spent chemicals

Which Fractionation Process?

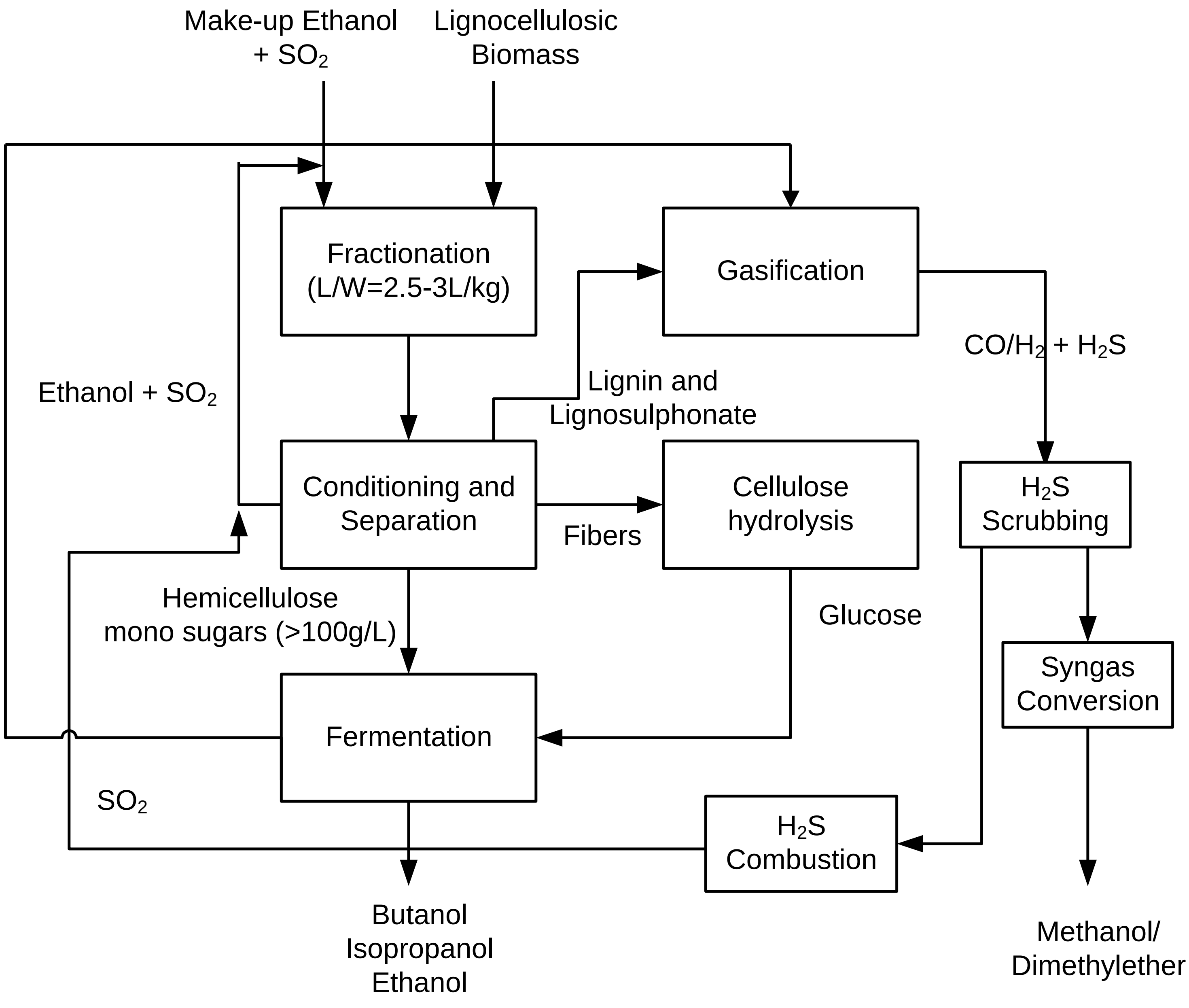
- Explosion pulping (high energy, SO_2 recovery, small particles)
- Auto hydrolysis (sticky lignin precipitates)
- Alkaline treatment (degradation of hemis)
- Acid hydrolysis (sticky lignin, acid recovery)
- Ethanol/ALCELL (high pressure)
- Sulfite process (slow, hemi oxidation, sulfur recovery, no resinous wood)
- SPORL (chemical recovery, hemi oxidation)

SO_2-EtOH-H_2O (AVAP®) Fractionation

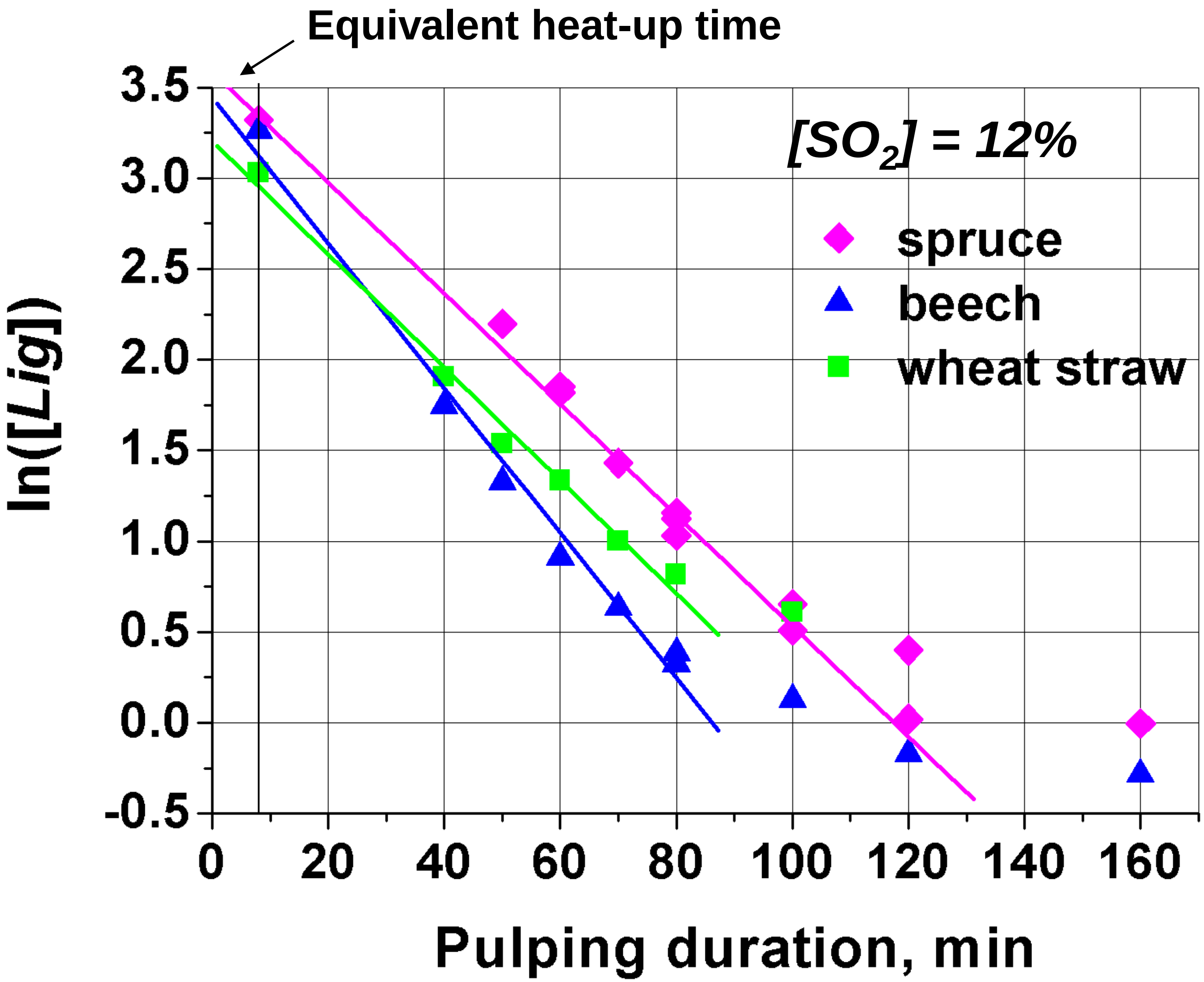
+ Omnivorous (due to SO_2)
+ > 100 g/L hemi monosugars (due to SO_2)
+ No separate impregnation (due to EtOH)
+ No oxidation of sugars to acids (due to no base)
+ No sticky lignin (due to SO_2 and EtOH)
+ Simple recovery of SO_2 and ethanol, allowing smaller economical scale (due to no base)
+ Wide range of final products (due to SO_2)
+ Easy cellulose hydrolysis (rel. high purity fibers)

AVAP™ pulping/biorefining is employed by API

Integrated Process for Biofuels



Omnivorous Delignification



Feedstocks and AVAP Fractionation

Spruce chips | **SW biomass** | **HW biomass** | **DIP**



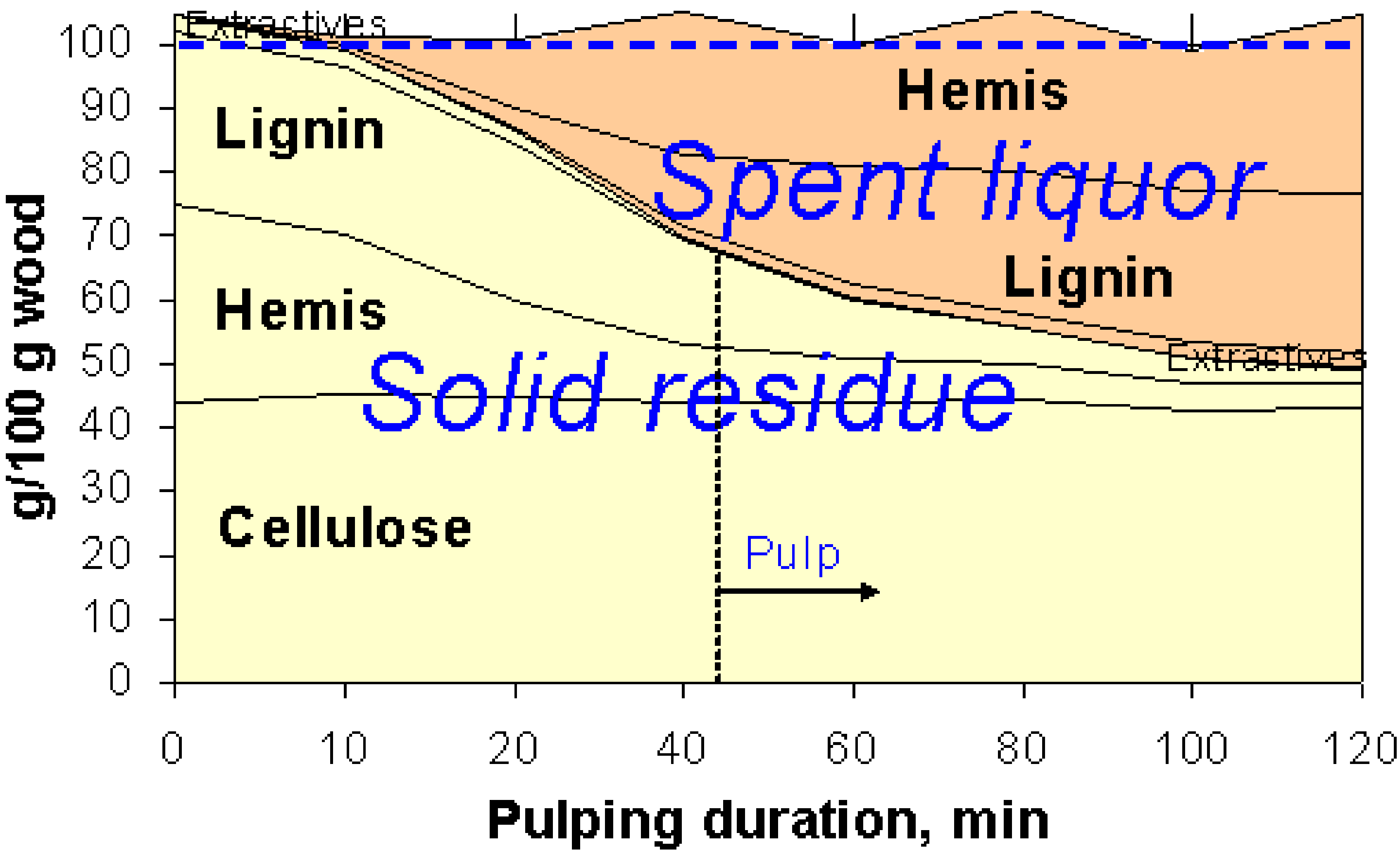




Pulp for papermaking!

***Fractionation at 135ºC for 80 min, 12% SO_2**

No Oxidation of Hemicelluloses



Different Pulps by Adjusting [SO_2]

Initial [SO_2] in the liquor, %	wood	3.0	6.0	12
Kappa number	-	32.6	34.4	32.2
Yield, %	-	46.9	49.9	51.6
Intrinsic viscosity, mL/g	-	586	937	1070
Composition, g/100 g wood				
Cellulose	40.9	40.6	41.0	41.3
Glucomannan	16.2	2.25	3.82	4.20
Xylan	5.44	0.91	1.54	1.88
Lignin	27.7	2.81	3.15	3.30

Spruce; T = 135 °C, Time variable, L/W = 6 L/kg

Effect of L/W on Spruce Pulping
(12% SO_2, 135°C, 80 min)

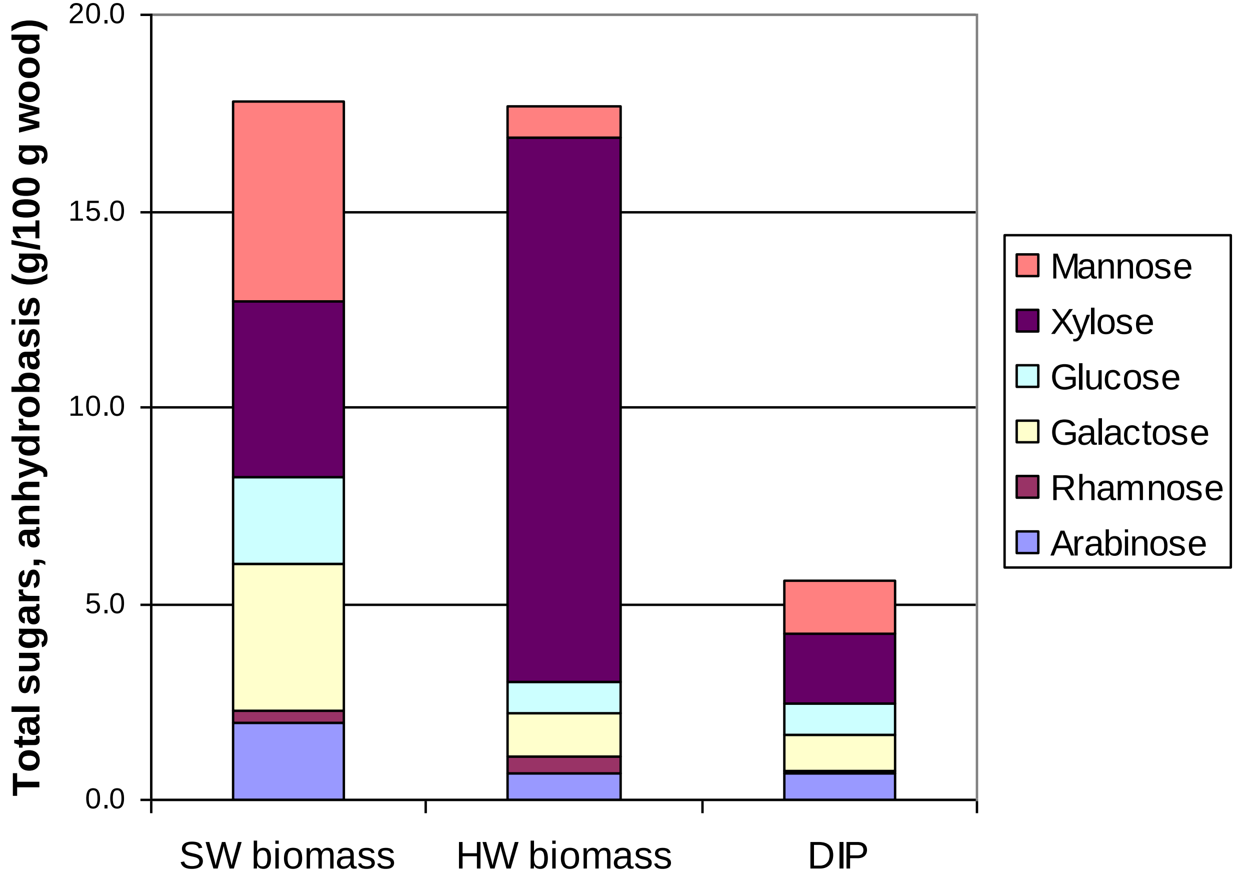
L/W, L/kg	6	3	2	1
SO_2, % on wood	72	36	24	12
Pulp yield, %	51.5	50.0	49.8	55.4
Kappa no.	33.5	34.8	44.7	n.m.
Lignin, % on wood	3.14	3.12	3.94	9.01

- **Pulp properties do not change for L/W from 6 to 3.**

- **Lower L/W gives lower delignification due to SO_2 depletion**

- **However, L/W of 2 may be possible with increased [SO_2]**

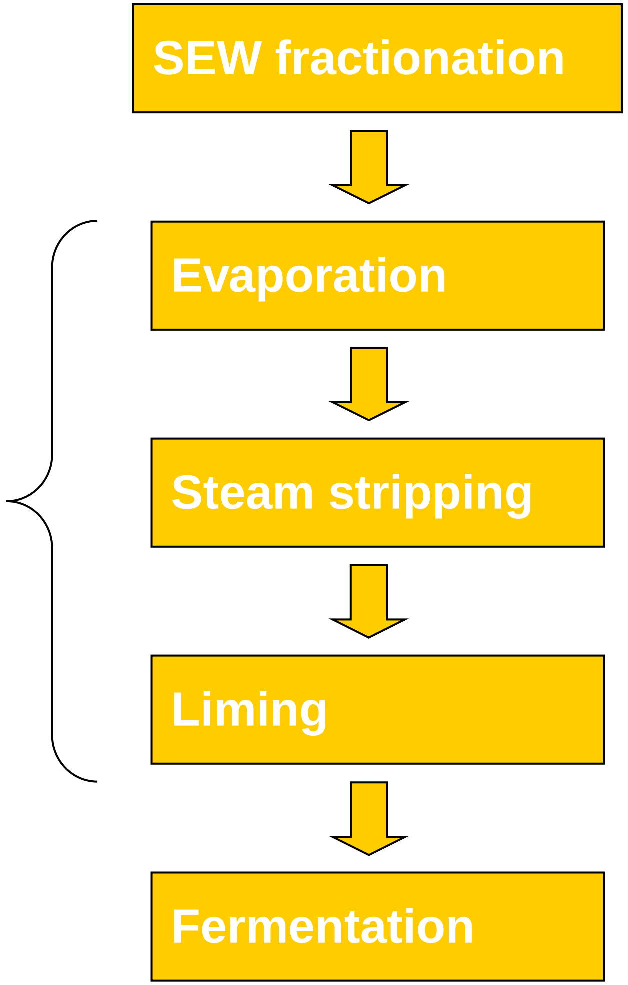
Sugars in Biomass Spent Liquors



***Fractionation at 135°C for 80 min, 12% SO_2**

Conditioning Process

- Recovery of EtOH + SO_2 by evaporation to approx. 65% weight loss
- Further removal of SO_2 by steam stripping
- Neutralization of liquor with $Ca(OH)_2$
- Final conditioning for complete elimination of SO_2 when making butanol



Effect of Conditioning

- Evaporation increases sugar concentration:
  - From the original 20 g/L up to over 100 g/L
  - However, about 15% sugar loss is observed
- Monosugars/Total sugars increases:
  - From initial 50% to over 90%
- Removal of SO_2 and EtOH are efficient:
  - EtOH recovery > 99% to < 0.5 g/L
  - SO_2 removal > 99.9% wt. to < 5 ppm
- HMF only 0.3g/L and furfural not detectable

Pretreatment/fractionation Comparison

Measure	Steam Expl	EtOH	SPORL	AVAP
Spent Liquor Mono Sugars	Spruce	Lobl. Pine	Spruce	Spruce
Glucose (kg/ dry ton wood)	100	35	68	17
Mannose (kg/ dry ton wood)	78	62	112	73
Enzymatic Yield of Fibers (FPU)	26	20	24	-
Glucose+Mannose(kg/od ton wood)	346	347	372	455
Total Glu. + Man. (kg/ton)	524	444	552	545
Total Energy (MJ/dry ton wood)	1980	1250	1500	730
Temperature (°C)	215	170	180	135
L/W (m^3/dry ton wood)	1.0	3.0	3.0	2.0
Heating (MJ/dry ton wood)x 50%	1800*	1070	1140	550
Chipping (MJ/dry ton wood)	180	180	180	180
Defibration (MJ/dry ton wood)	0	0	180	0
Efficiency (kg monosugars/MJ)	0.26	0.36	0.37	0.75

J.Y. Zhu and X.J. Pan Bioresource Technology 101 (2010) 4992–5002

Conclusions

- Several commercial forest biorefineries within 5 years
- Uses omnivorous lignocell. fractionation integrated within forest mill to overcome scale disadvantage with petro-refinery
- SO_2-EtOH-H_2O (AVAP®) fractionation process has great potential
- Chemrec-type gasification is an enabling technology for the biorefinery