3AV6.7

Ductile Bioplastics and Lignite-grade Fuel from Cellulosic Biomass

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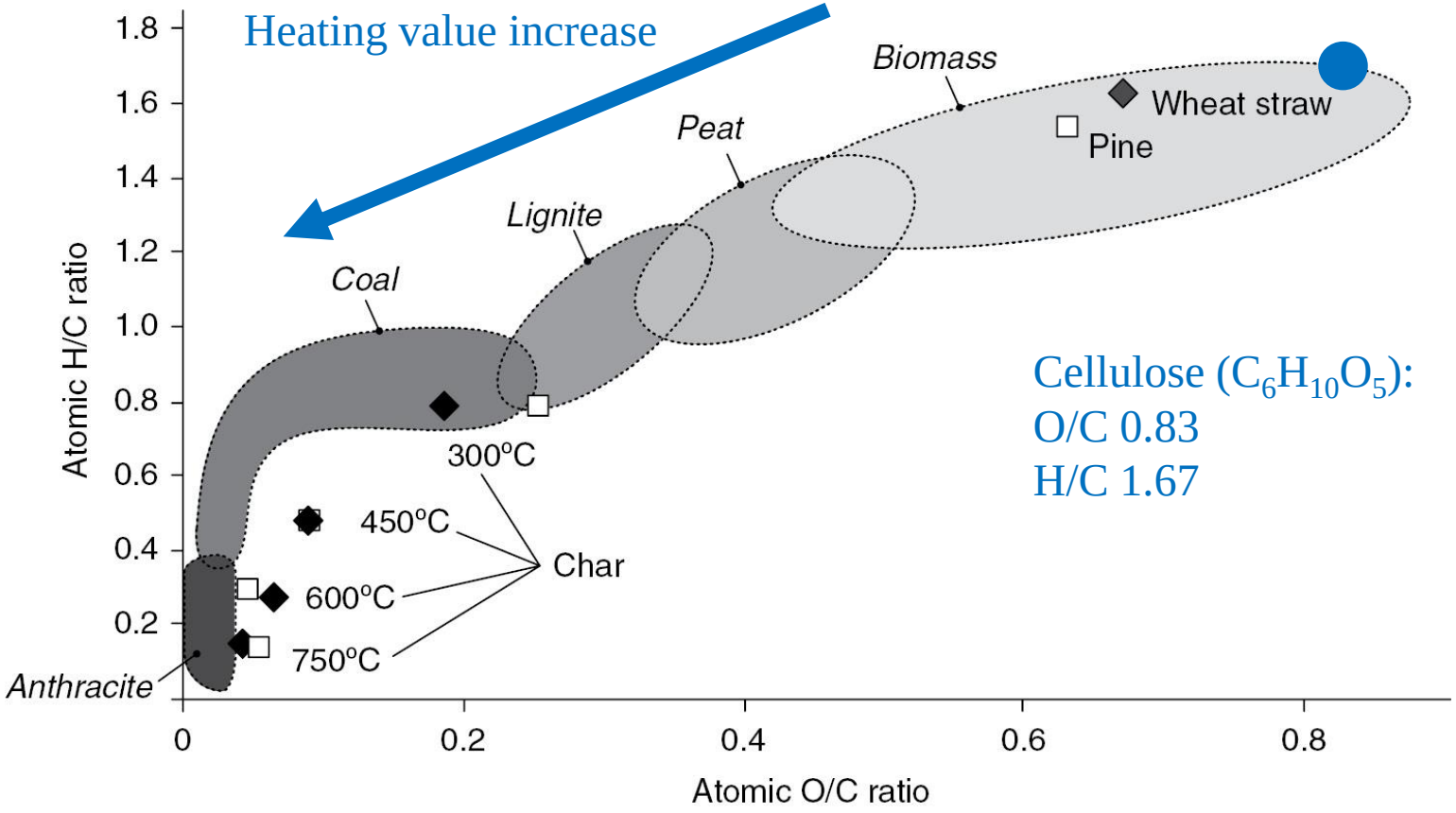
1. Cellulose is a Poor Solid Fuel



Cellulose ($C_6H_{10}O_5$):
O/C 0.83
H/C 1.67

Solid Fuel	Anthracite	Coal	Lignite	Biomass
Typical HHV (MJ/kg)	35	29	22	19
Average price ($/ton)	100	60	20	60

2. Cellulose for Value-added Products

Thermal catalytic hydrolysis and conversion (TCHC) of cellulose into levulinic acid and formic acid in water
(catalyst, 150-200 ^{o}C, 14-20 atm)

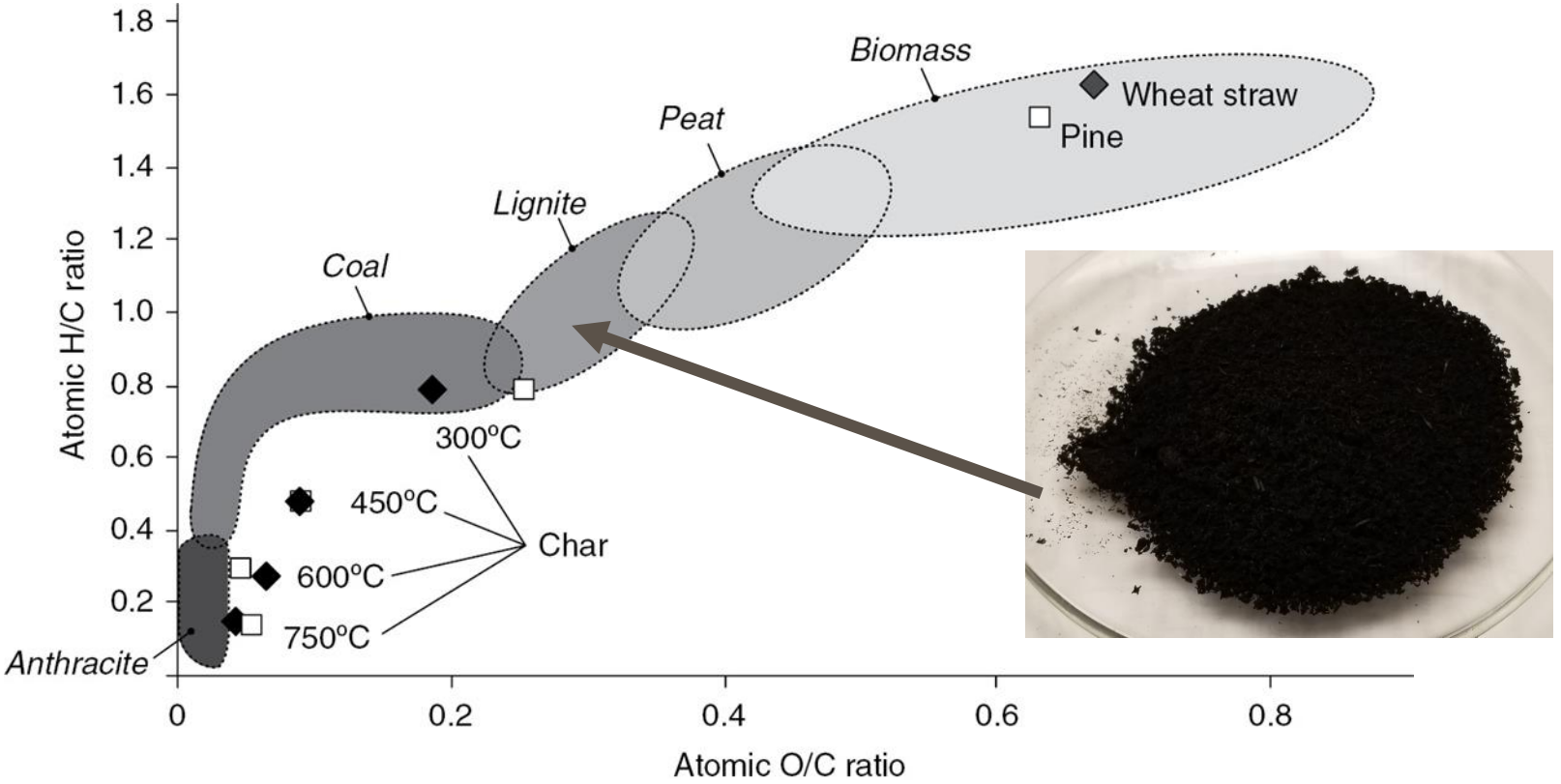
- Cellulose → Levulinic acid + Formic acid + **Humins**
  $C_6H_{10}O_5$ (162 kg) → $C_5H_8O_3$ (116 kg) + CH_2O_2 (46 kg)

- Theoretical yield: 100% w/w
  Real yield: 40-60% theoretical

- Two types of products from TCHC reaction:

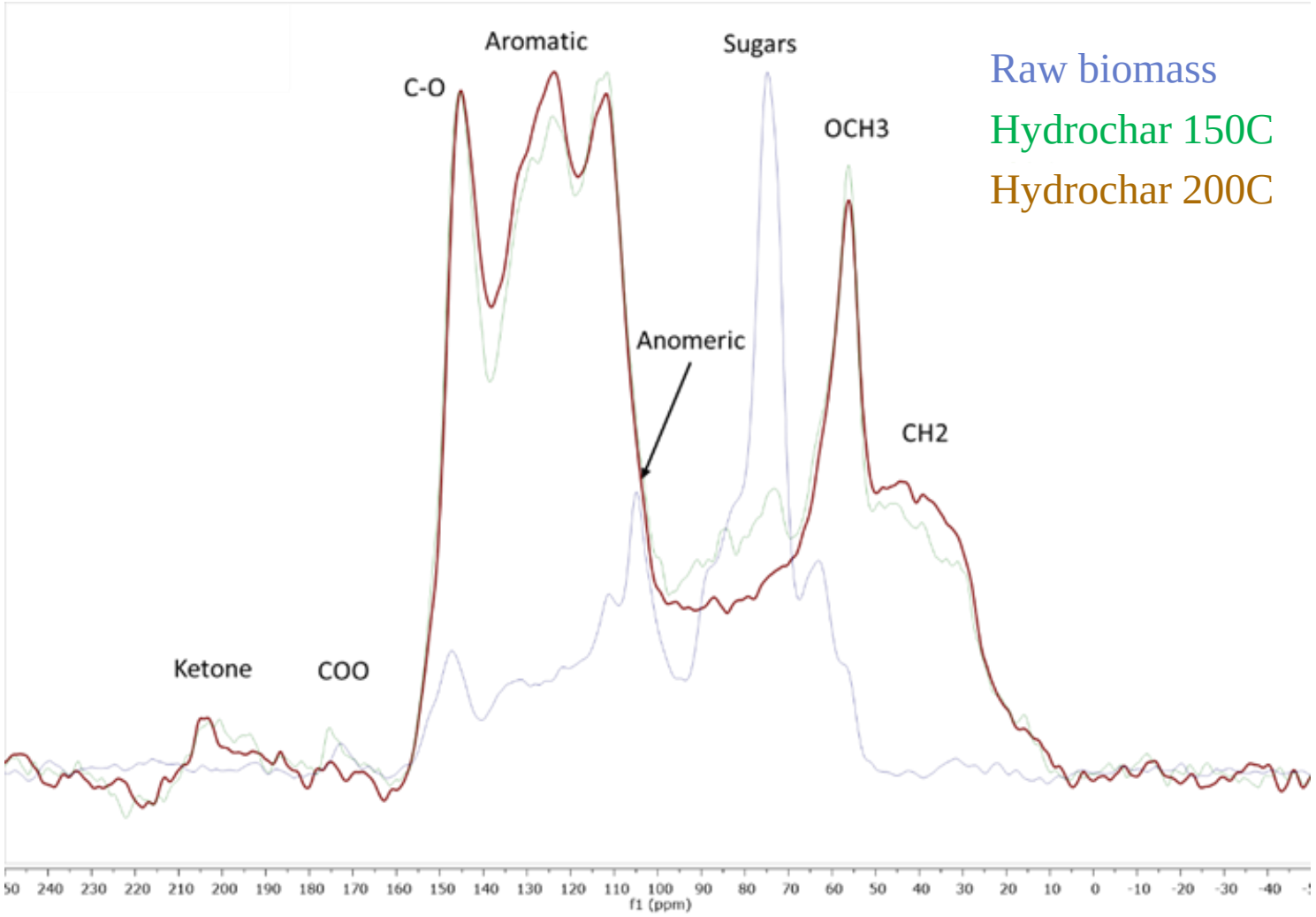
1. Hydrochar (carbonized residue)
2. Hydrolysates of cellulose, hemicellulose and extractives

3. Hydrochar Better than Raw Wood Fuel

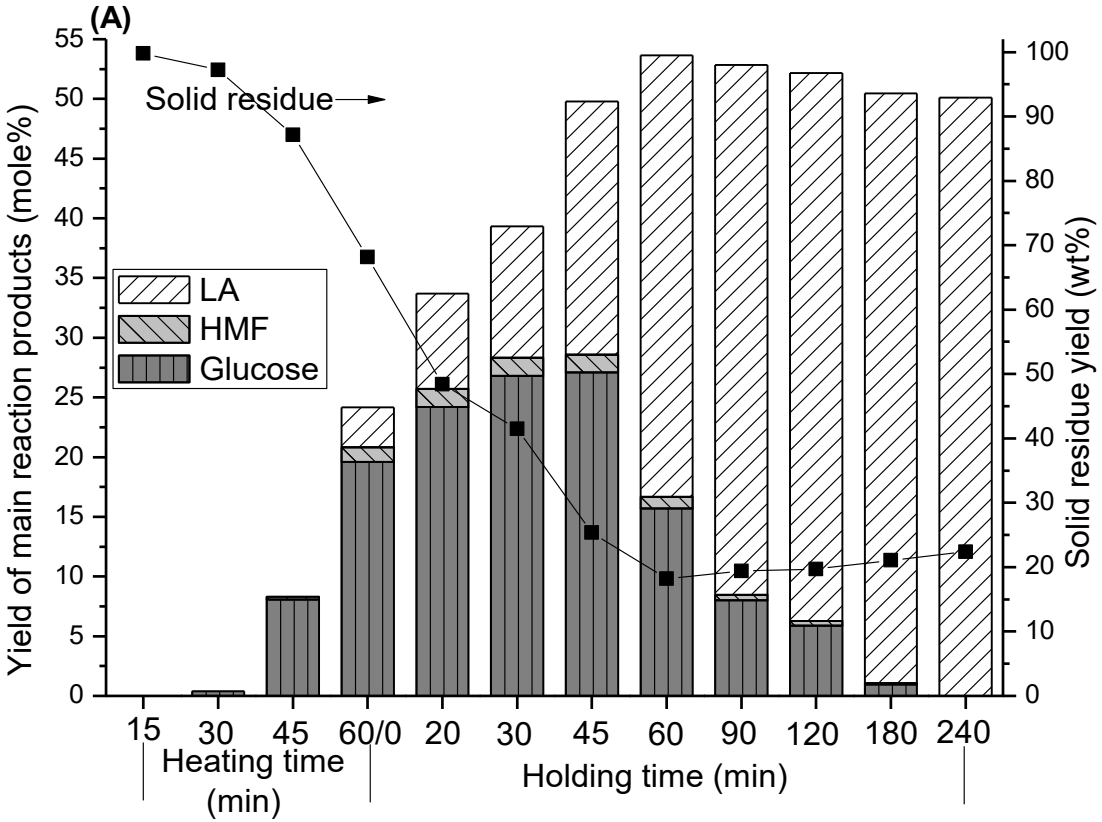


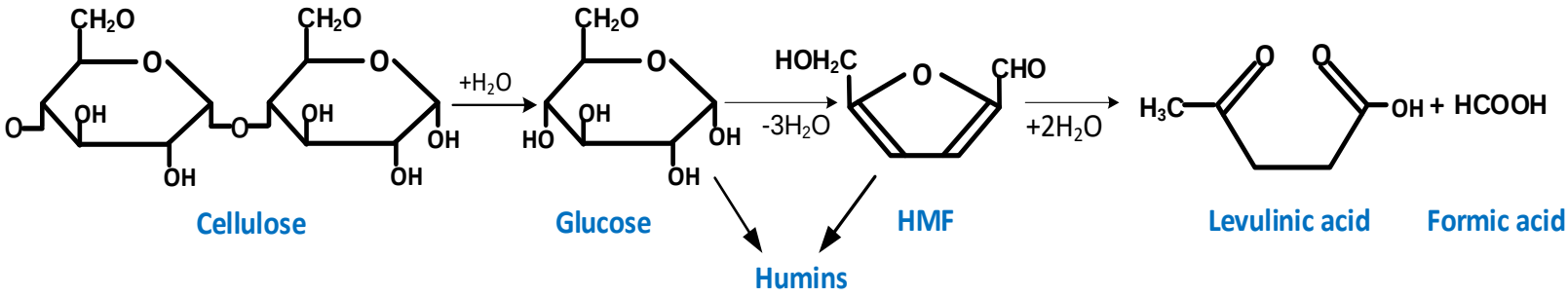
Solid fuel	Yield (wt%)	H/C (-)	O/C (-)	HHV (MJ/kg)	HHV Enhanced	Price ($/ton)
Raw wood	100	1.55	0.65	19	1	130
Hydrochar	47	0.96	0.31	27	1.42	185

4. Solid State 13C NMR of Hydrochar

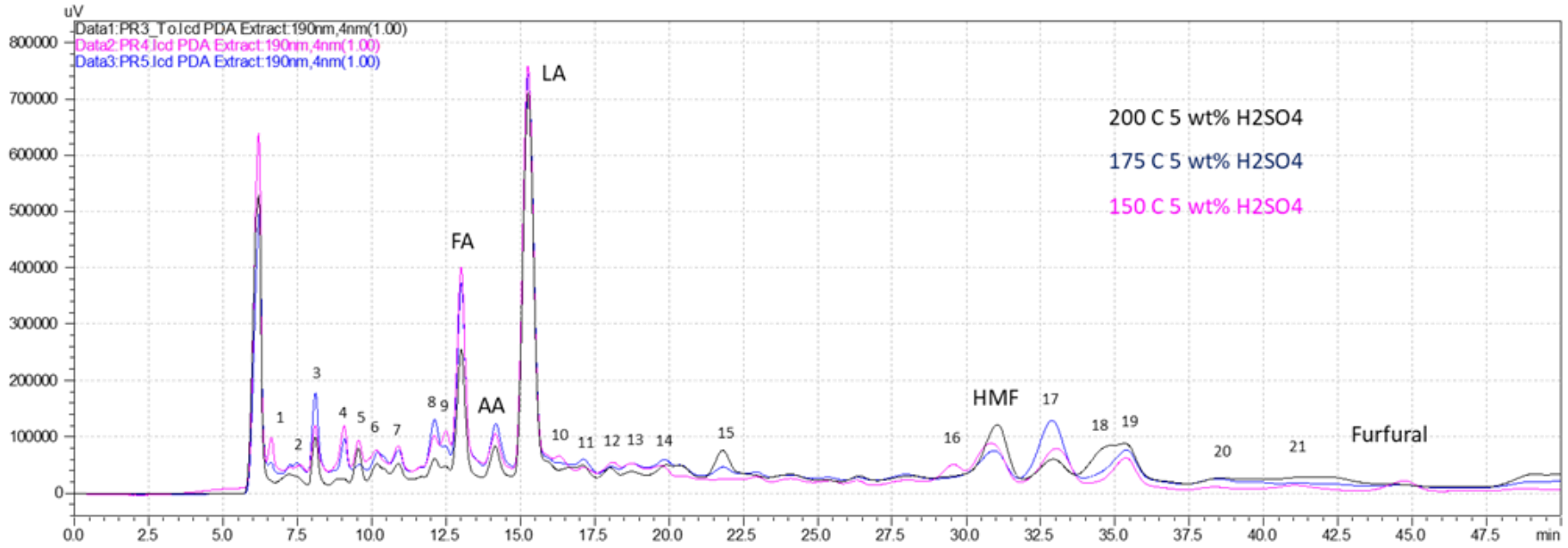


5. Cellulose to Levulinic and Formic Acids





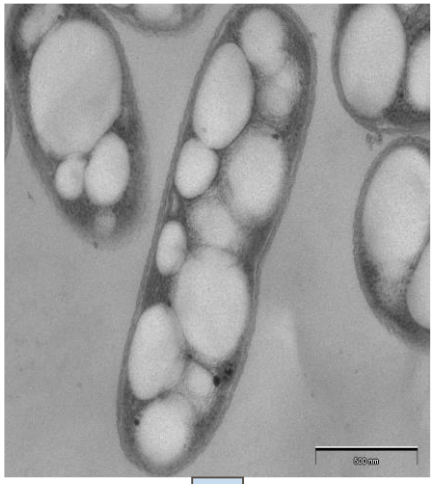
6. Hydrolysate Solution of Sawdust



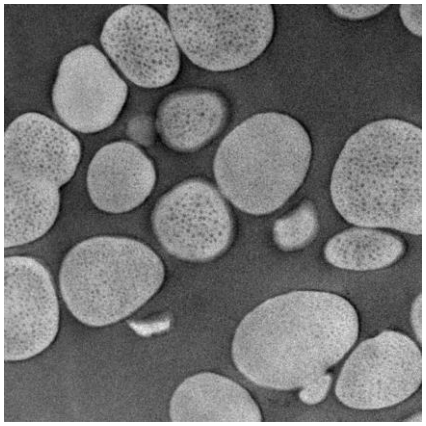
- Levulinic acid (LA) and formic acid (FA) are major compounds
- Biological conversion by microbes:
  to use organic acids (LA, FA, AA)
  to form valuable products (bioplastics $4/kg)
  to facilitate products recovery from aqueous solution

7. PHA Bioplastics from Hydrolysates

Levulinic acid
Acetic acid
Formic acid
Others



Residual Cell Mass
(RCM ~80% protein)

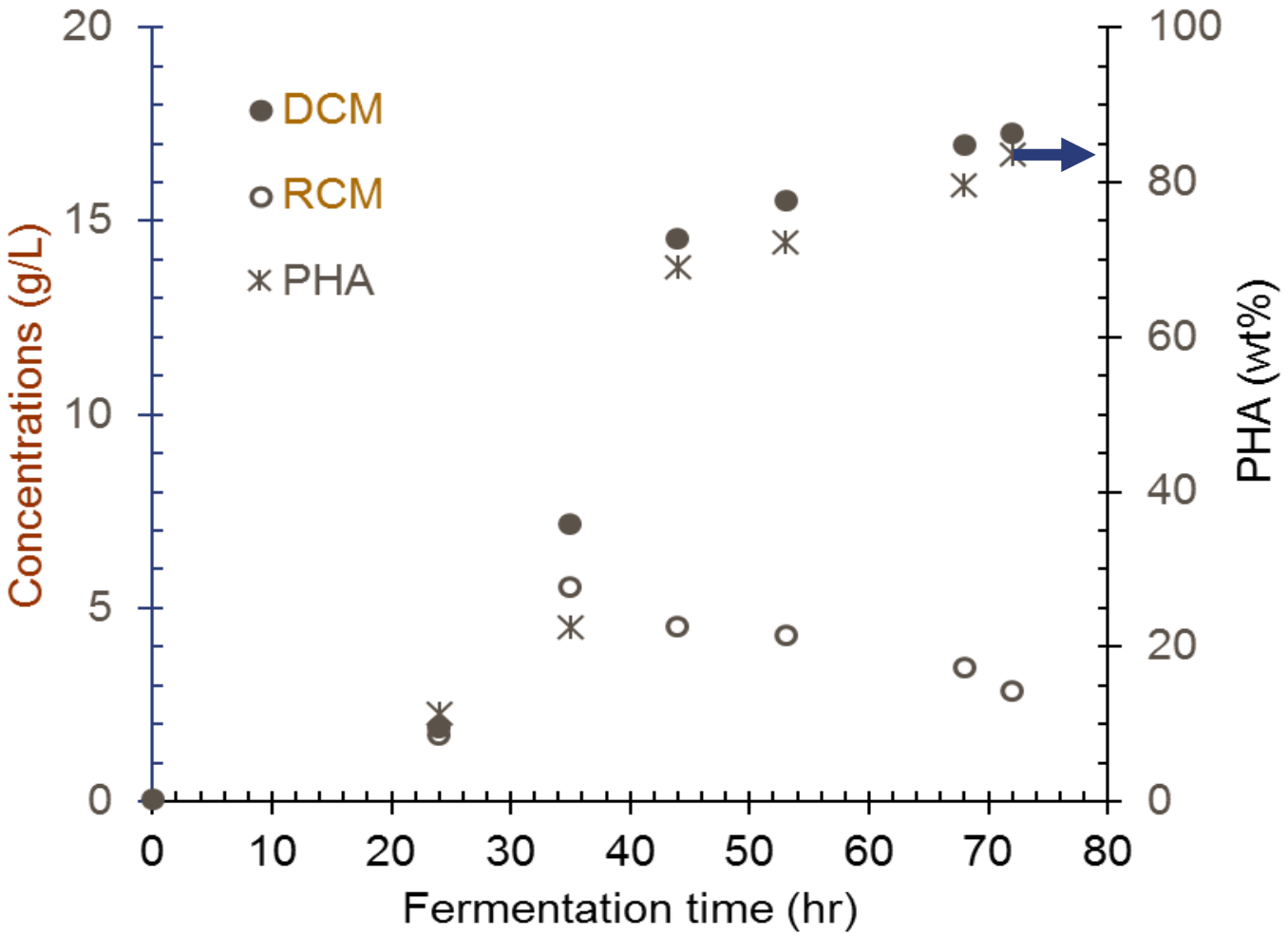


Microgranules

PHA Bioplastics

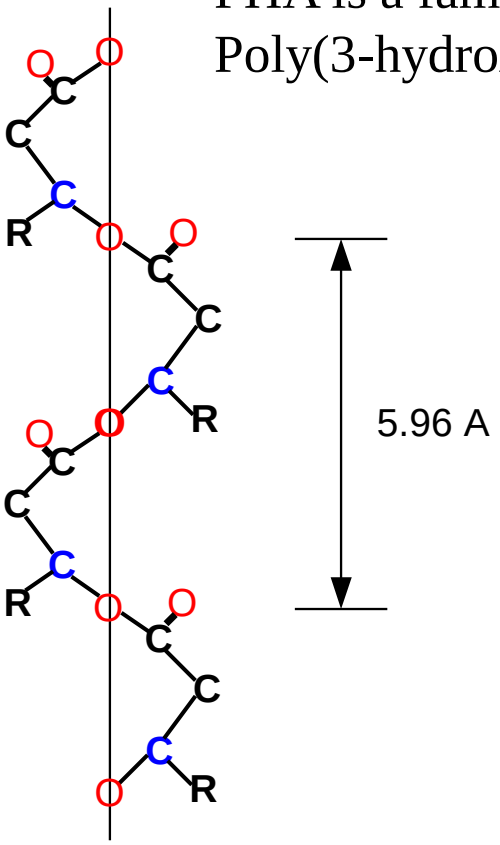
8. High PHA Content in Microbial Cells

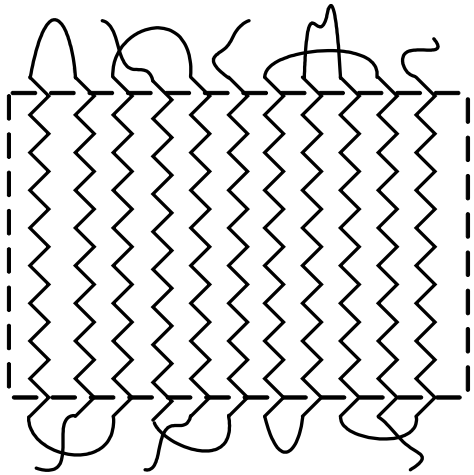
DCM: dry cell mass; RCM: residual cell mass

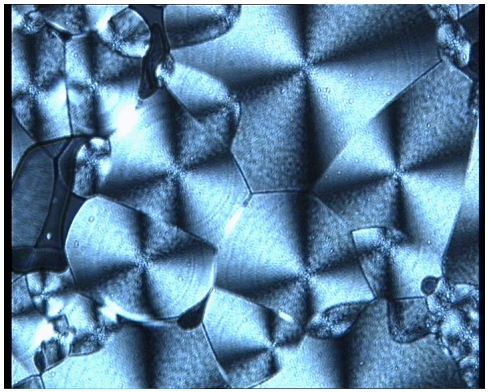


9. What is Polyhydroxyalkanoate(PHA)?

PHA is a family of biopolyesters as microbial energy reserve
Poly(3-hydroxybutyrate)(P3HB) is a representative member



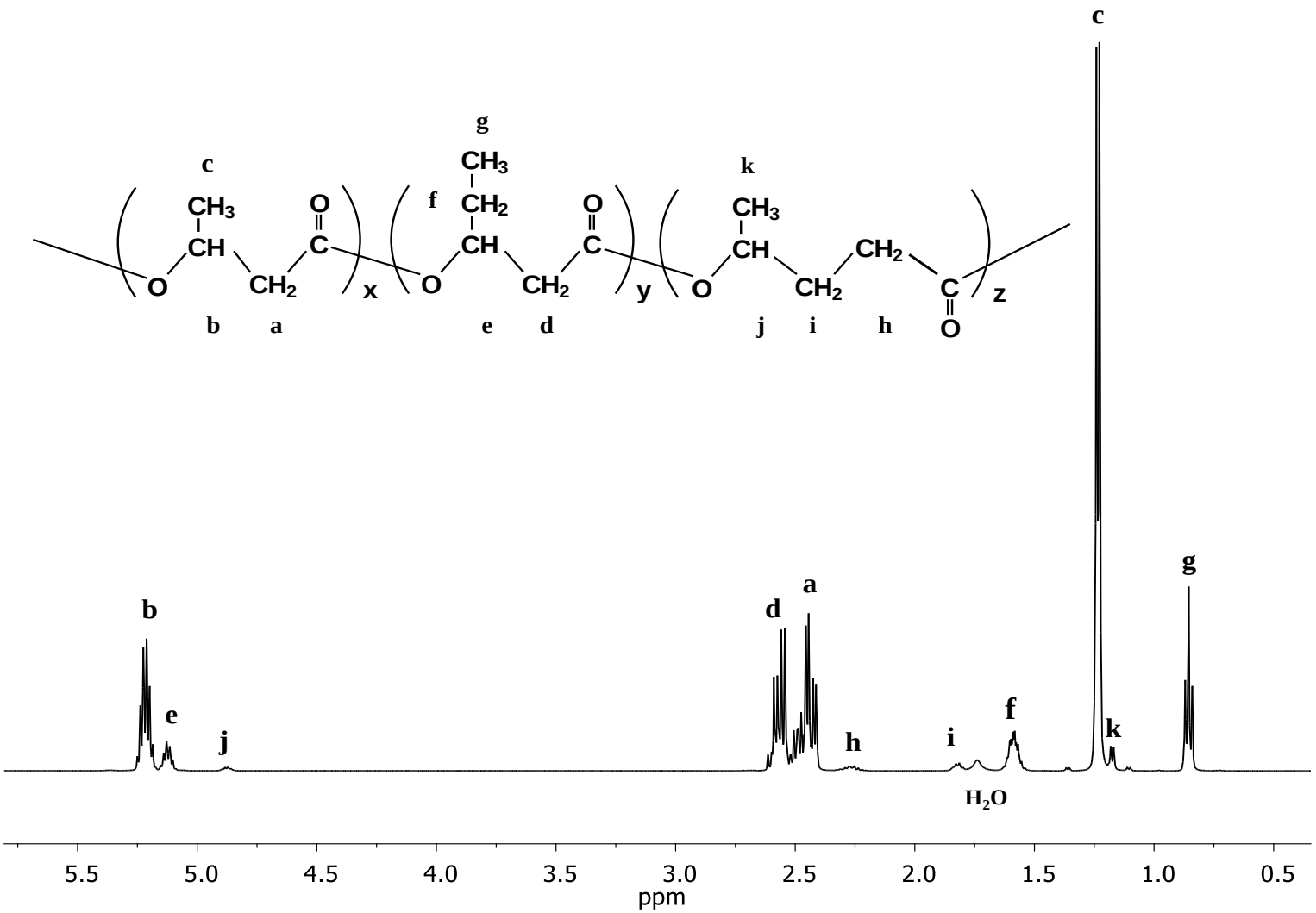




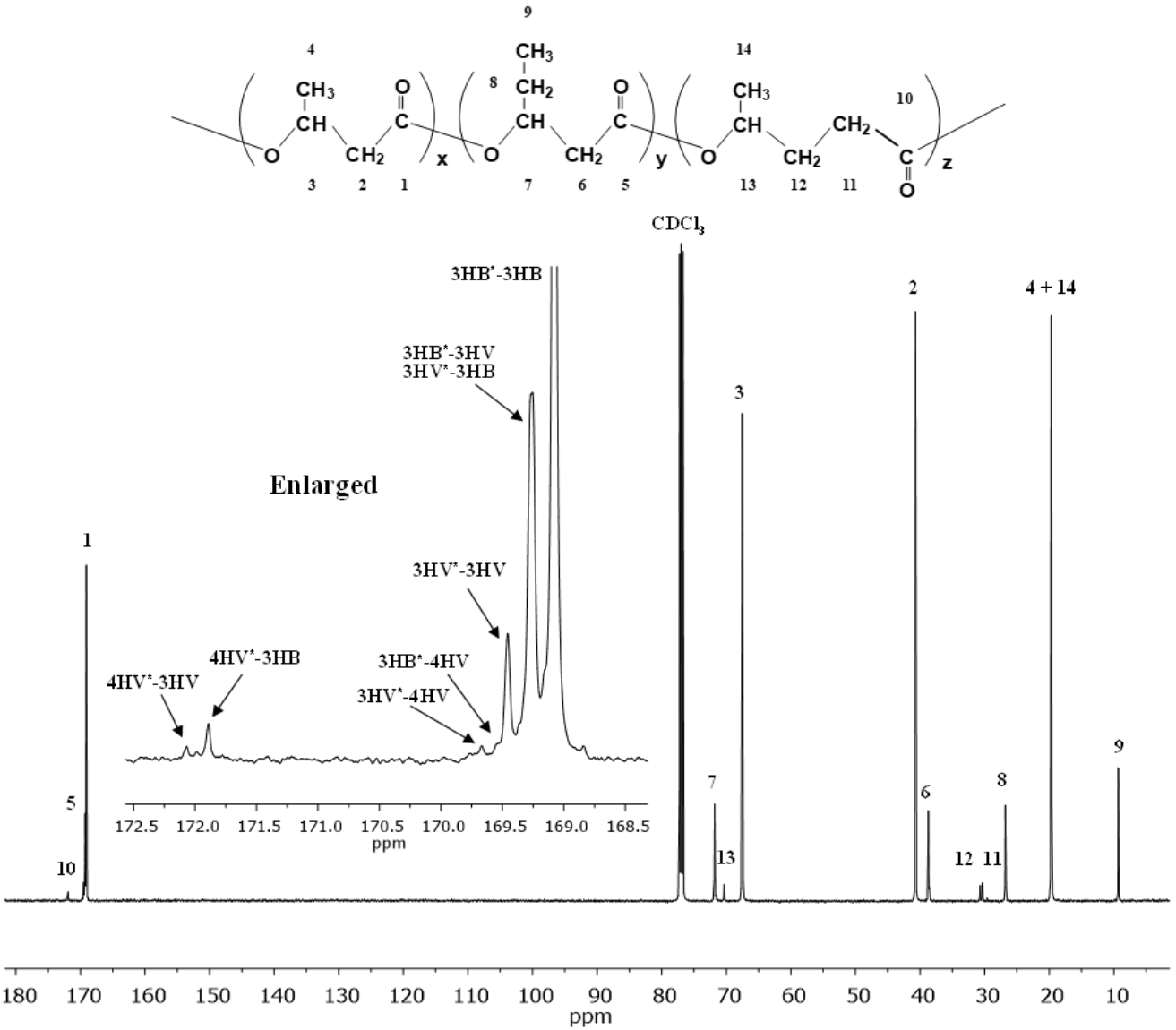
R: CH_3 (P3HB)
CH_2CH_3 (P3HB3HV)
$CH_2CH_2CH_3$ (P3HB3HHx)

- P3HB has a high crystallinity (60-70%)
- P3HB becomes brittle with time!
- Control the post-crystallization effect by reducing crystallinity

10. ^{1}H NMR of P(3HB-3HV-4HV)



11. ^{13}C NMR: Random 4HV in Terpolyesters



12. Rigid versus Ductile PHA Bioplastics

Commercial P3HB,P(3HB3HV) and P3HB3HHx versus P3HB3HV4HV

PHA	3HB mol%	3HV mol%	3HHx mol%	4HV mol%	Tg °C	Tm °C	Xc %	E %	Tensile MPa
P(3HB)	100	-	-	-	4	176	70	5	43
P(3HB3HV)	90	10	-	-	-1	140	60	50	20
P(3HB3HHx)	90	-	10	-	-1	127	34	400	21
P(3HB3HV4HV)	54	43	-	3	-4	78	31	500	23

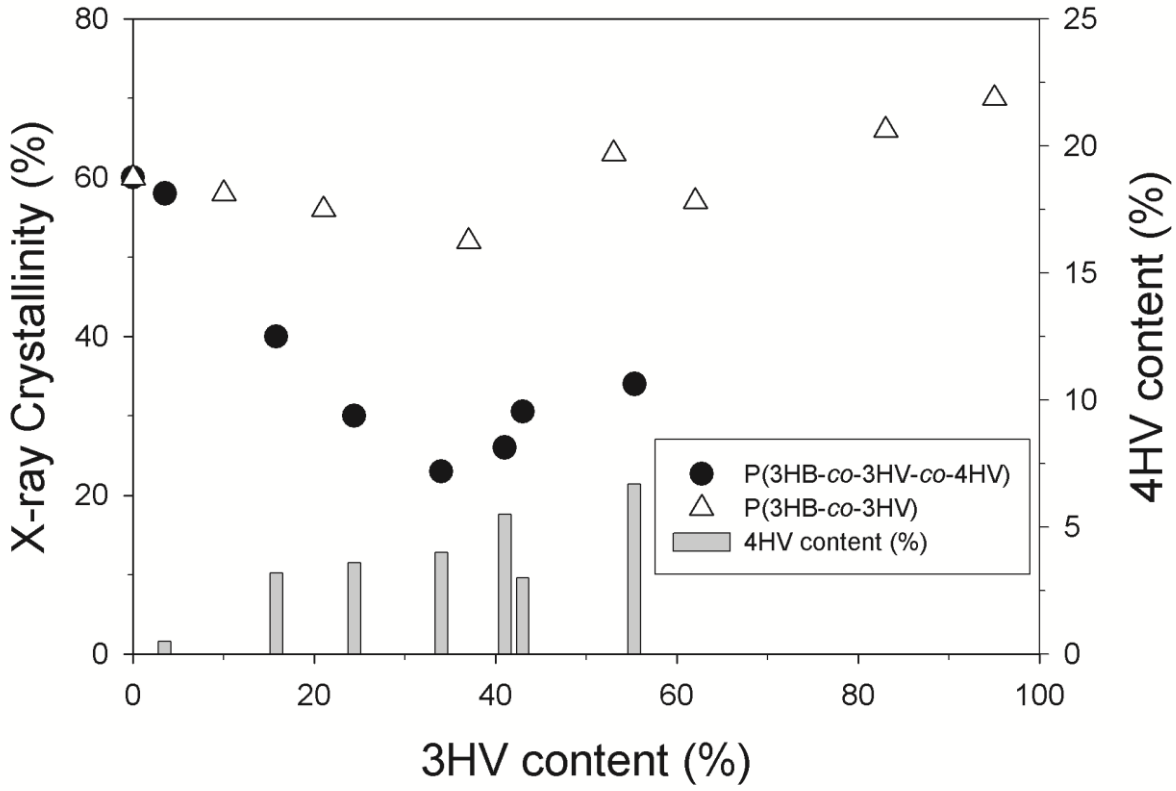
P3HB3HV4HV is a flexible natural plastic.

Is the reduced crystallinity and high ductility attributed to 3HV or 4HV?

13. Effect of 4HV on P3HB3HV4HV Crystallinity

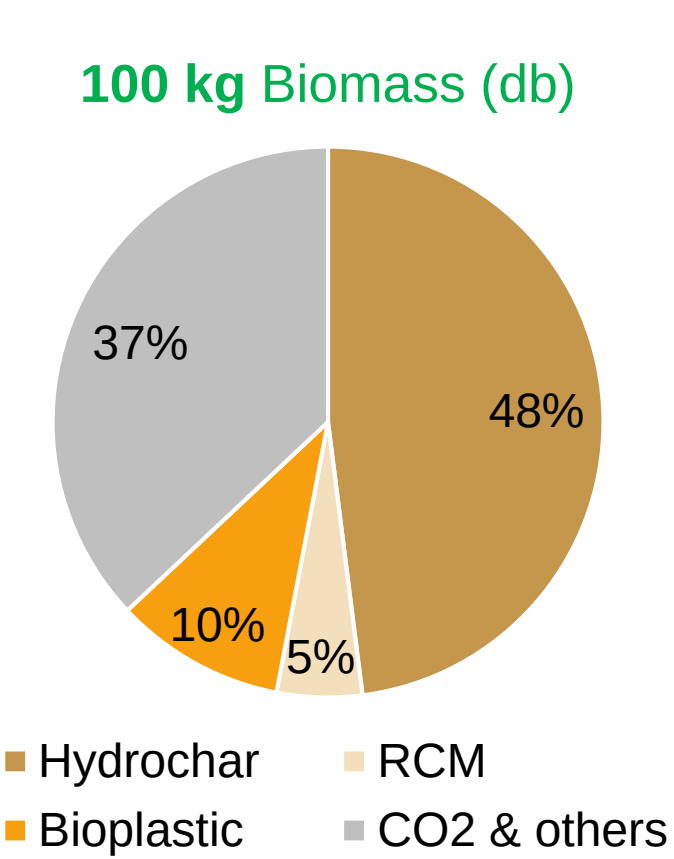
P3HB crystalline

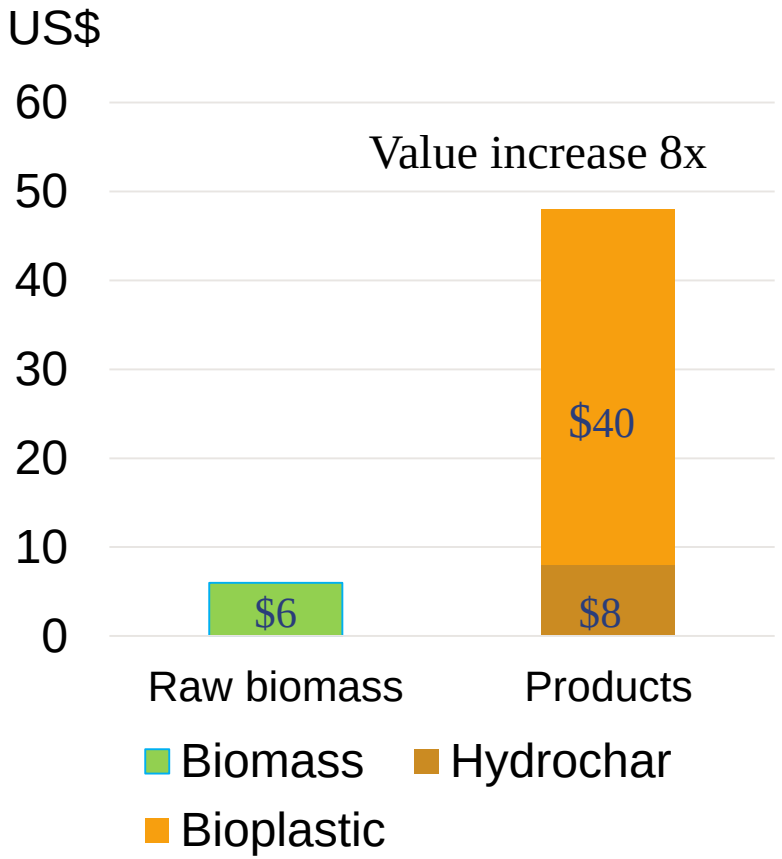
P3HV crystalline



- 3HV has a moderate effect on the crystallinity of P3HB3HV
- The minor 4HV is the defecting points in P3HB3HV crystalline, resulting in low crystallinity and high ductility of P3HB3HV4HV

14. Valorization of Cellulosic Biomass





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Thank You!!!

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