# Axioms

**If you are making a molecule from another molecule, you are a chemist, doing chemistry.**

Synthetic biology is merely chemistry conducted by other means.
"Bio" doesn't change anything.

**Think outside the fermentation tank.**

You do not always need fermentable carbon.

**Don't re-invent the reaction.**

There are 150 years of organic chemistry available,
and pharma and oil have already paid for it.

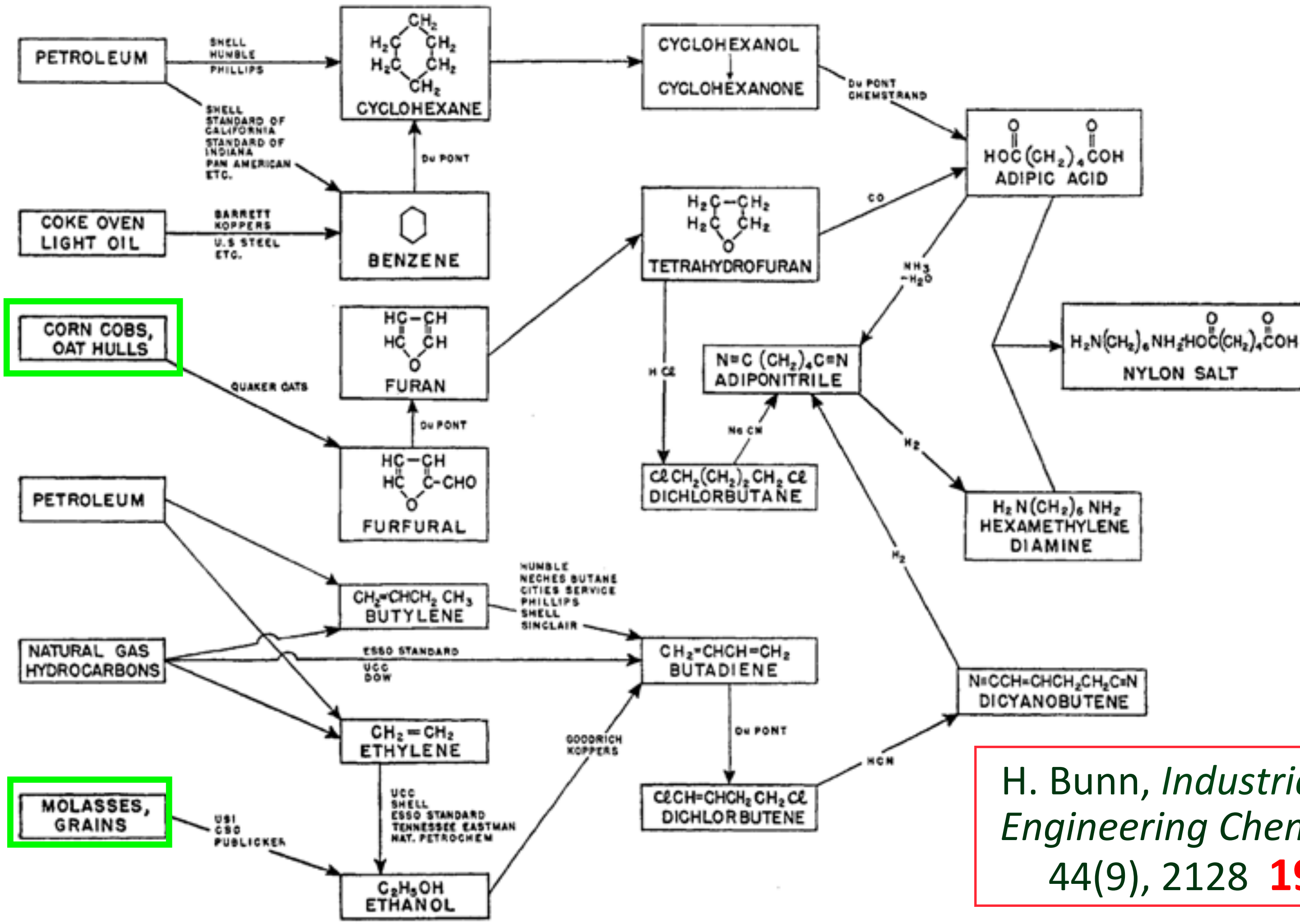
# ....and Provocations

**If you want to capture solar energy,
the worst method is photosynthesis.**

**If you want to capture $CO_2$ from the atmosphere,
the best method is photosynthesis.**

**The best use of biomass is to make materials,
structural and chemical.
Not fuels.**

# We Have Done This Before

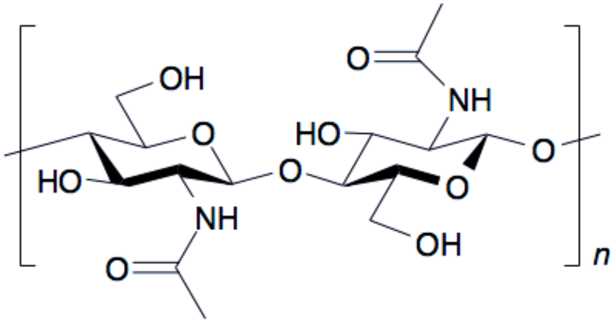



H. Bunn, *Industrial and Engineering Chemistry,* 44(9), 2128 **1952**

# Biomass Chemicals - the big ones
## annual global volumes

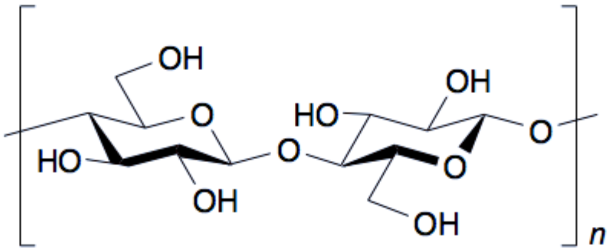
**Chitin ~70 - 100,000 Mt**

More than cellulose




**Cellulose 70,000 Mt**

Nano-cellulose crystals probably occur in any deconstruction process

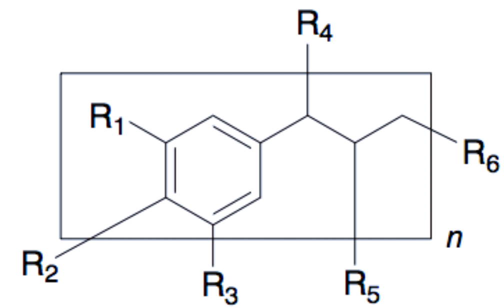


## Lignin 30,000 Mt

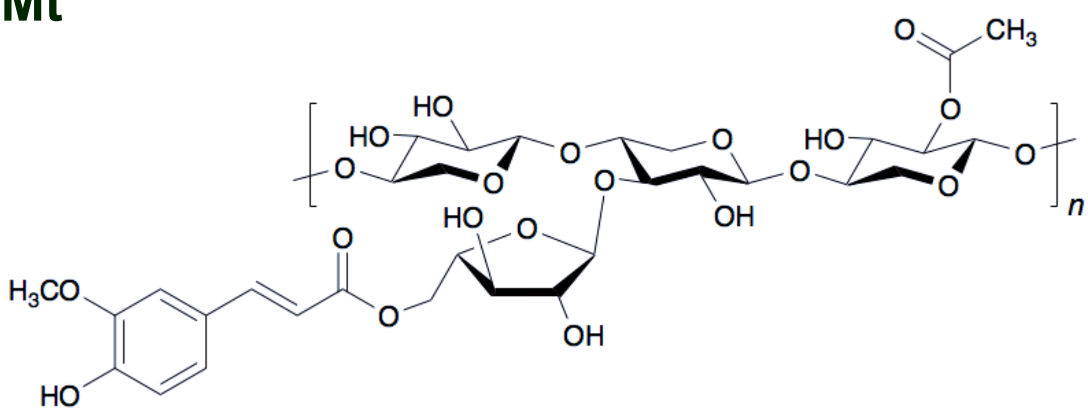
By weight, there is enough to satisfy global aromatic chemicals

$R_1$ = H, OH, $OCH_3$
$R_2$ = OH, OCH-
$R_3$ = $OCH_3$, Ph
$R_4$ = OH, OCH-, OPh
$R_5$ = OH, OCH-, OPh
$R_6$ = OH, OCH-




## Hemi-cellulose 36,000 Mt

Very heterogeneous, but easily obtained



# More Polymers - the next biggest

| | |
|---|---|
| **Polyethylene** | 95 Mt |
| **Polypropylene** | 60 Mt |
| **PET** | 56 Mt |
| **Polystyrene** | 20 Mt |
| **Polyacrylates** | 12 Mt (est) |
| **Polyamides** | 6 Mt |
| **ABS** | 6 Mt |
| **PLA** | 1.2 Mt (2020) |

# And the monomers that make them

| | | |
|---|---|---|
| **Ethylene** | 200 | Mt (annual global production) |
| **Propylene** | 90 | Mt |
| **Styrene** | 30 | Mt |
| **MEG** | 26 | Mt |
| **Acrylic Acid** | 9 | Mt |
| **Acrylonitrile** | 6.5 | Mt |
| **Caprolactam** | 6.3 | Mt |
| **BDO family** | 4.5 | Mt |
| **Methylmethacrylate** | 4.5 | Mt |
| **Adipic Acid** | 3 | Mt (1.4 Mt HMDA to PA66) |
| **Lactic Acid** | 1.9 | Mt (2020 est) |
| | | |
| **BTX** | 117 | Mt |
| **Benzene** | 50 | Mt |
| **Toluene** | 25 | Mt |
| **Xylenes** | 42 | Mt (31 MMt pX to PET) |

**~ 510 Mt total**

# Is there enough biomass ?

## Disposition of Crude Oil in the US, 2017

| | 000's BBLS | | |
|---|---|---|---|
| | | | |
| Crude Oil & Petroleum Products | 7,255,119 | | 100.00% |
| | | | |
| Finished Motor Gasoline | 3,401,309 | | 47% |
| Distillate Fuel Oil | 1,437,312 | | 20% |
| Kerosene-Type Jet Fuel | 613,790 | | 8% |
| | | | |
| Natural Gas Plant Liquids and Liquefied Refinery Gases | 947,826 | | 13% |
| Propylene | 114,454 | | 1.6% |
| Ethane/Ethylene | 444,659 | | 6.1% |
| Normal Butane/Butylene | 12,782 | | 0.2% |
| Isobutane/Isobutylene | 50,329 | | 0.7% |
| Pentanes Plus | 36,882 | | 0.5% |
| | | | |
| Still Gas | 250,818 | | 3.5% |
| Petroleum Coke | 117,113 | | 1.6% |
| Asphalt and Road Oil | 128,739 | | 1.8% |
| Petrochemical Feedstocks | 128,224 | | 1.8% |
| Residual Fuel Oil | 130,889 | | 1.8% |
| Lubricants | 39,740 | | 0.5% |
| Miscellaneous Products | 34,228 | | 0.5% |
| Special Naphthas | 19,093 | | 0.3% |
| Finished Aviation Gasoline | 4,120 | | 0.06% |
| Waxes | 1,845 | | 0.03% |

www.eia.gov/dnav/pet/pet_sum_snd_d_nus_mbbl_m_cur.htm

**Oil:** 43 MJ/kg energy content, 125 kg/bbl

7,255 Mbbl consumed annually

= $3.9 \times 10^{10}$ GJ consumed annually

of which 75% is finished transportation fuels

**= $2.9 \times 10^{10}$ GJ** (gasoline, diesel and aviation kerosene)

**Biomass:** 17.5 MJ/kg energy content

1.3 Bt annually renewable biomass (USDA/DoE report)

**= $2 \times 10^{10}$ GJ available annually**

Assuming 25% of the biomass is used for energy in the conversion process, leaves **$1.5 \times 10^{10}$ GJ**

## Not enough!

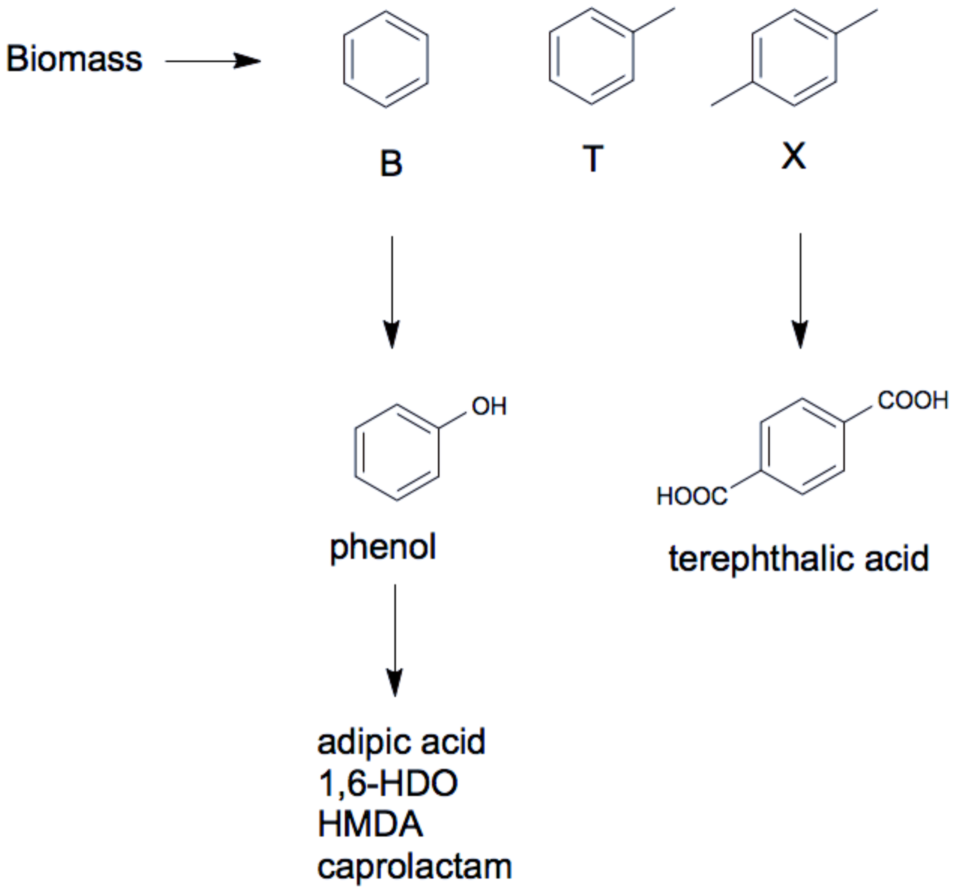
**But only 0.6 to $3.9 \times 10^{9}$ GJ of oil consumed as "chemicals"**

## <u>There is lots of biomass feedstock - *for chemicals*</u>

# Aromatics (BTX)

Thermal methods on intact cellulosic biomass lead to syn-gas and aromatics (methanol and BTX), or bio-crude that can fit into certain oil refineries

- Annelotech (BTX)
- UOP (pX from lignin)
- Bio-crude: Ensyn, Steeper, Canfor
- Virent/Tesoro/Andeavor/ Marathon



# Hemi-cellulose

**1000 t Hardwood**

- 450 t Cellulose
- 250 t Lignin
- 300 t Hemi-cellulose

**Hot water extraction** (www.absciences.com)

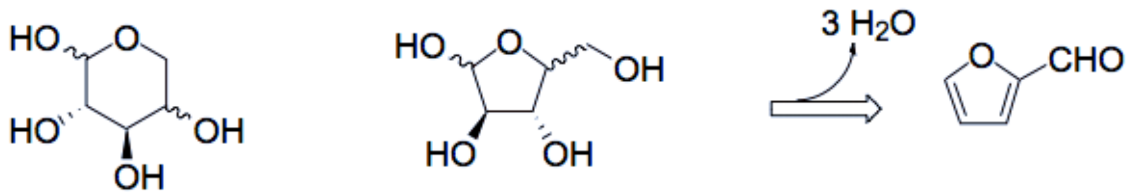
- 150 t extracted hemicellulose (50%)

**Conversion**

- 75 t furfural (80%)

The rest of the wood, ~770 t, is left physically intact
for pulp & pellets

# Old, Simple C5 Chemistry

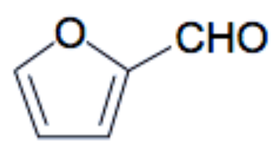



C5 sugars
(xylose / arabinose)
$C_5H_{10}O_5$

Furfural
$C_5H_4O_2$

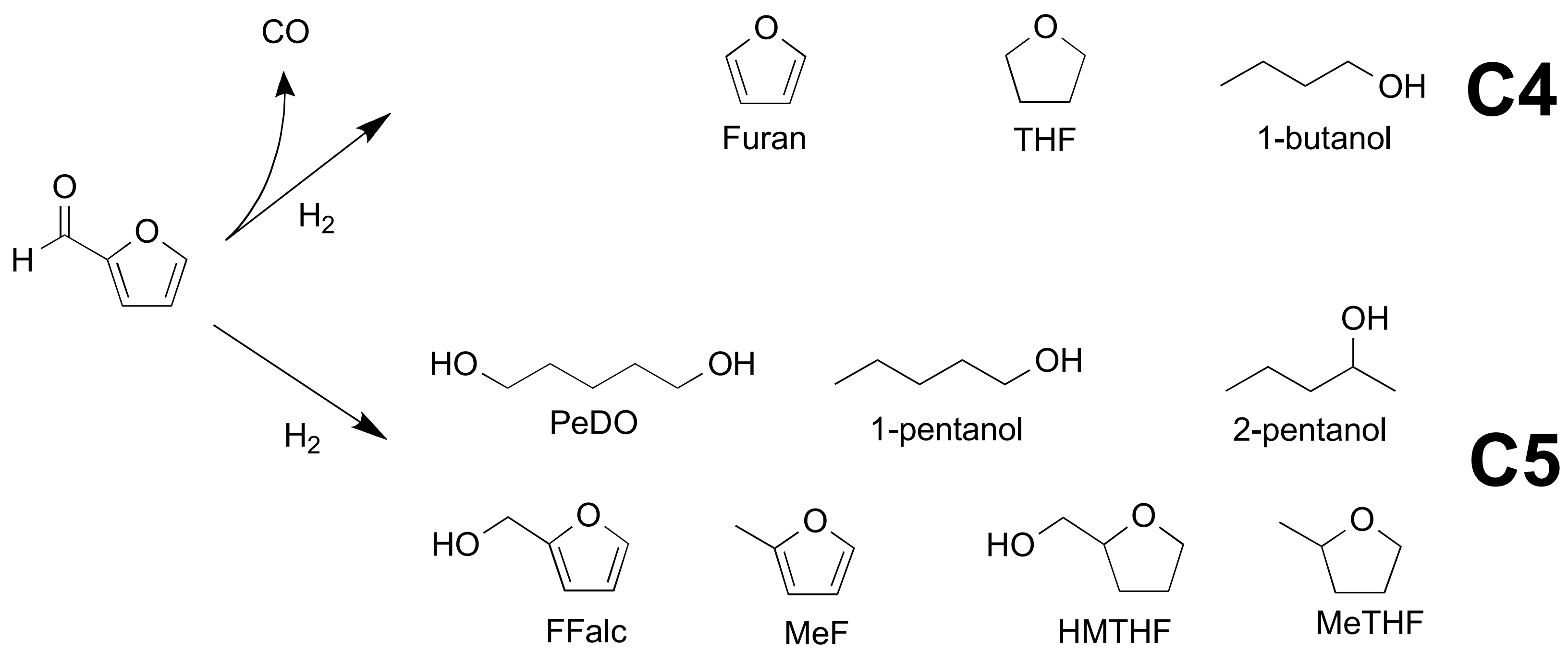
- Dehydration, usually acid-catalysed, of arabinoxylan to furfural has been practised industrially since 1880s
- No loss of carbon, no change of oxidation state, functionalized, aromatic
- C5 material *not available* from petrochemical C5 (cyclopentadiene)

cyclopentadiene
$C_5H_6$



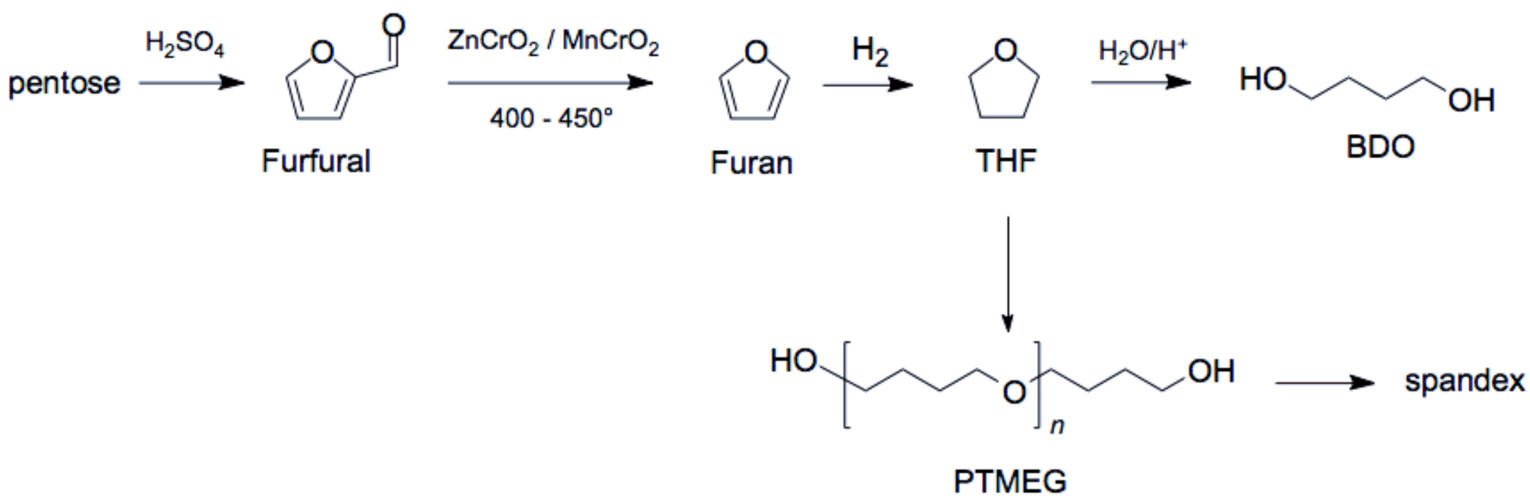

Furfural
$C_5H_4O_2$

# C5 Sugars



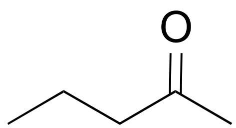

- A combination of three reactions:
  - decarbonylation, hydrogenolysis and hydrogenation
- We just need hydrogen and existing petrochemical reactor technology
- And a catalyst ..... but it must be stable!

# C5 for THF / BDO / PTMEG

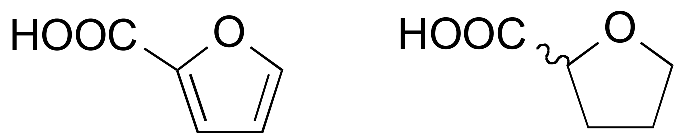


# Two More Reactions on C5

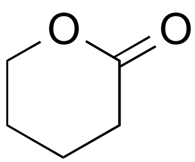
## Dehydration & Oxidation




2-pentanone

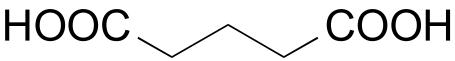



Furoic acids

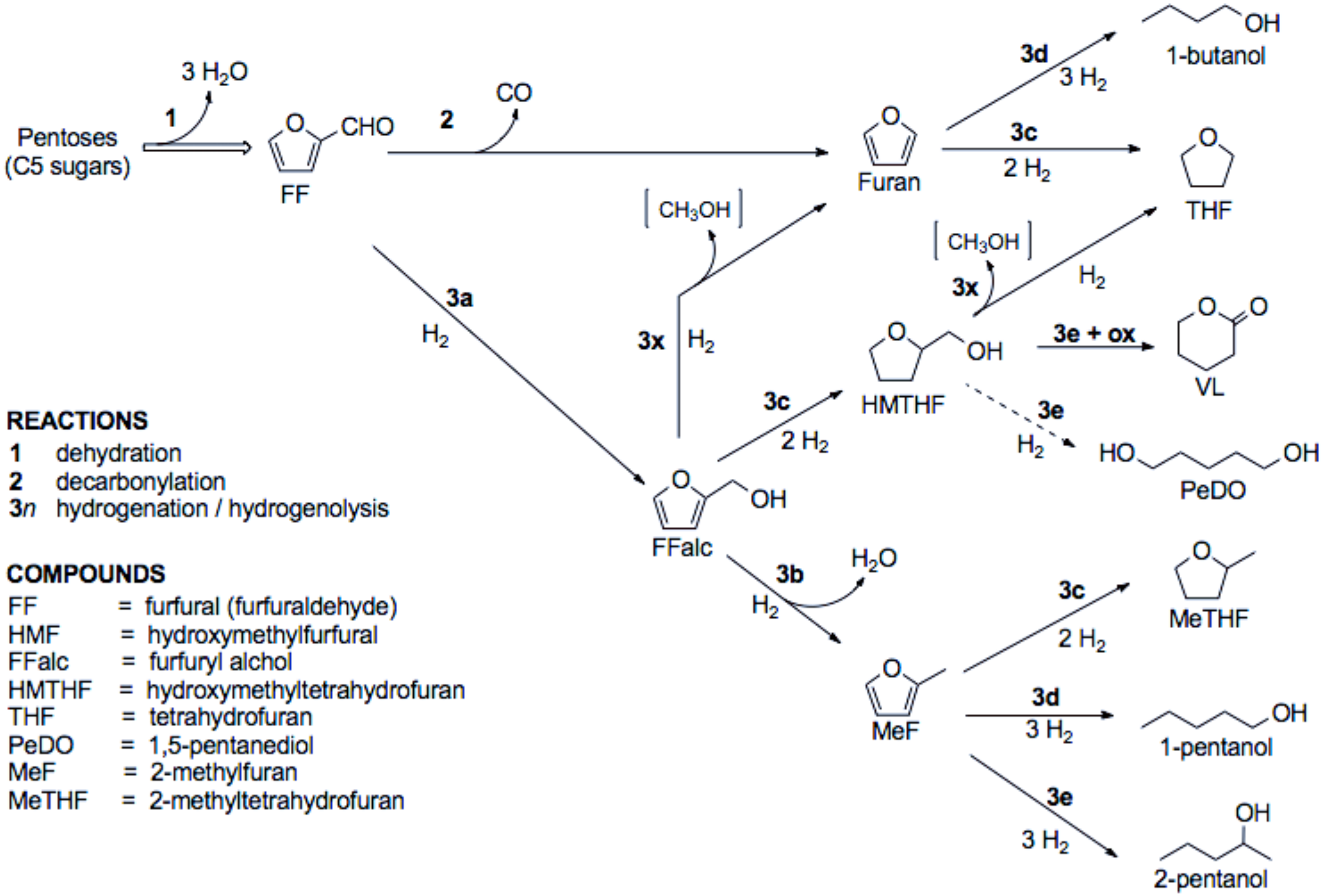



GBL

α-olefins




Glutaric acid




**REACTIONS**

**1** dehydration
**2** decarbonylation
**3*n*** hydrogenation / hydrogenolysis

**COMPOUNDS**

FF = furfural (furfuraldehyde)
HMF = hydroxymethylfurfural
FFalc = furfuryl alchol
HMTHF = hydroxymethyltetrahydrofuran
THF = tetrahydrofuran
PeDO = 1,5-pentanediol
MeF = 2-methylfuran
MeTHF = 2-methyltetrahydrofuran

WO2014152366A1

**Everything has been thought of before;**

**the problem is to think of it again.**

*Johann Wolfgang von Goethe*

David R. Dodds, Ph.D.
**Dodds & Associates LLC**
315 884 3703 **/** SKYPE daviddodds4 / TWITTER drdodds4
ddodds@techdiligence.net
www.techdiligence.net