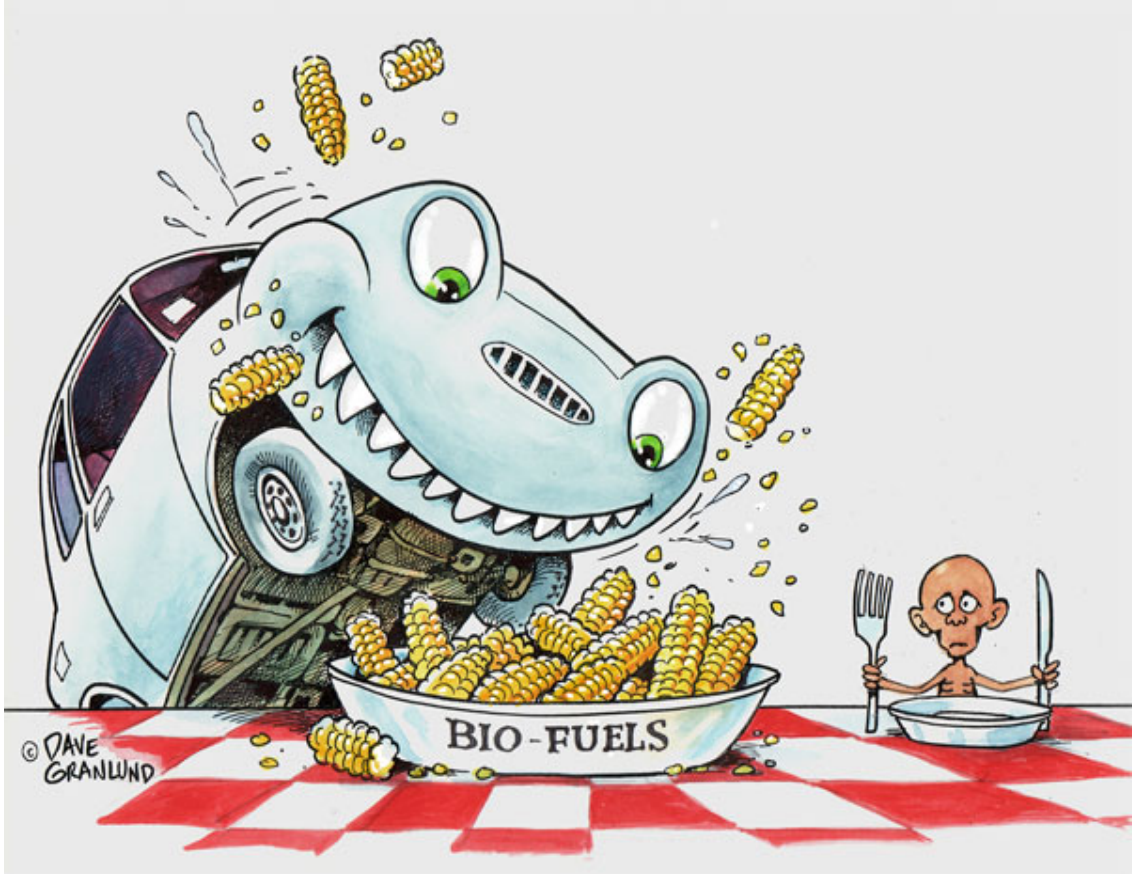
Catalytic Strategies for Biofuel Production



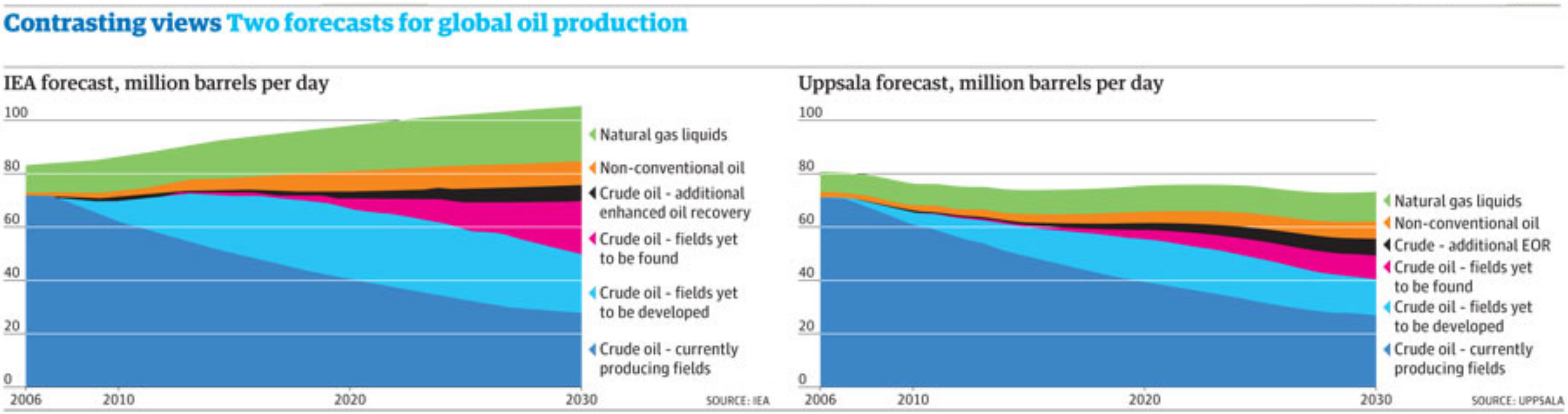
Jack Terrett
MacMillan Group Meeting
February 19th, 2015

Global Petroleum Supplies are Finite

- There is heated debate over the total global crude oil reserves

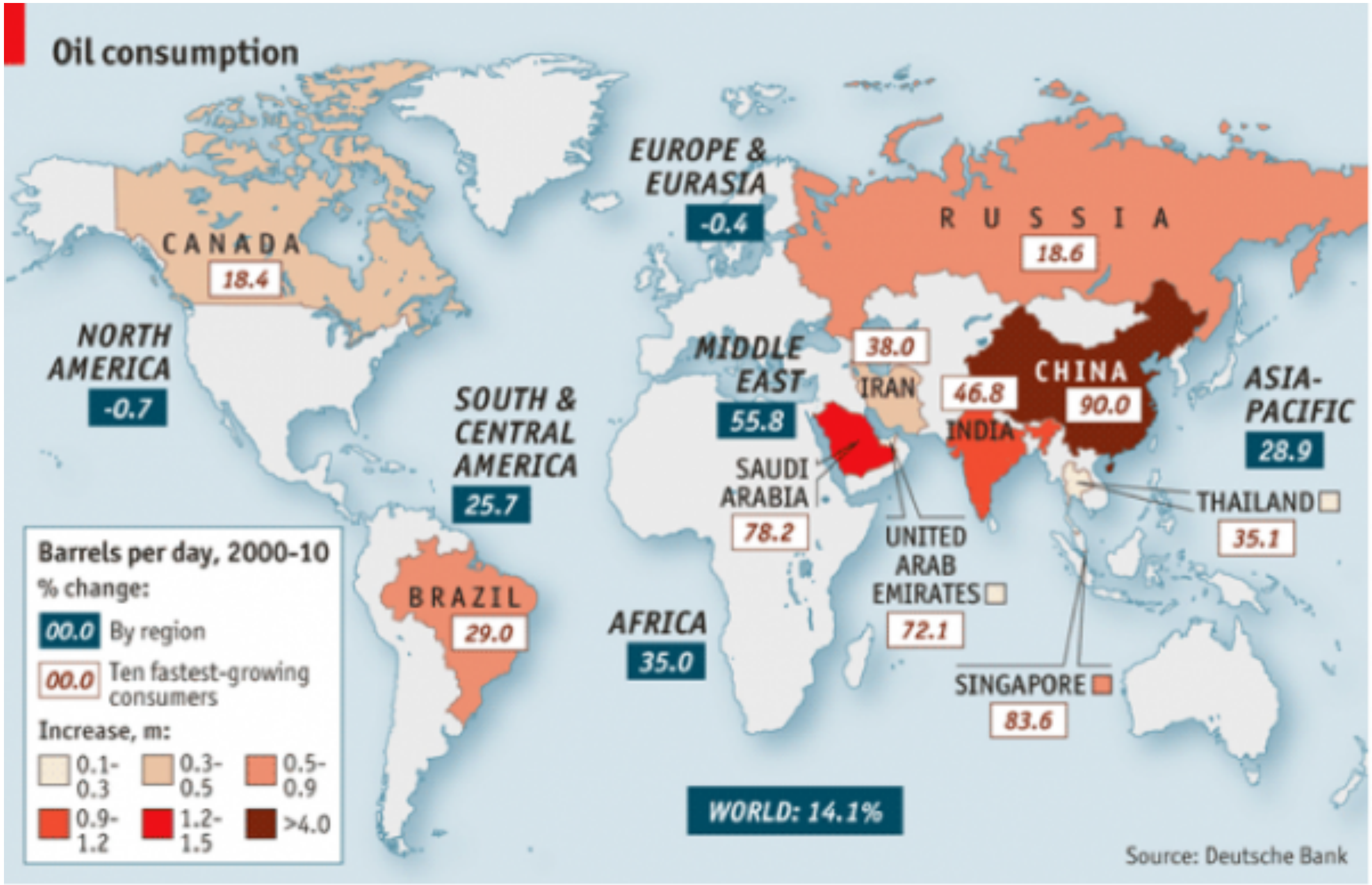
- Different models predict conflicting trends in oil production over the next 15 years

Regardless of short term, petroleum supplies are finite and will eventually run out



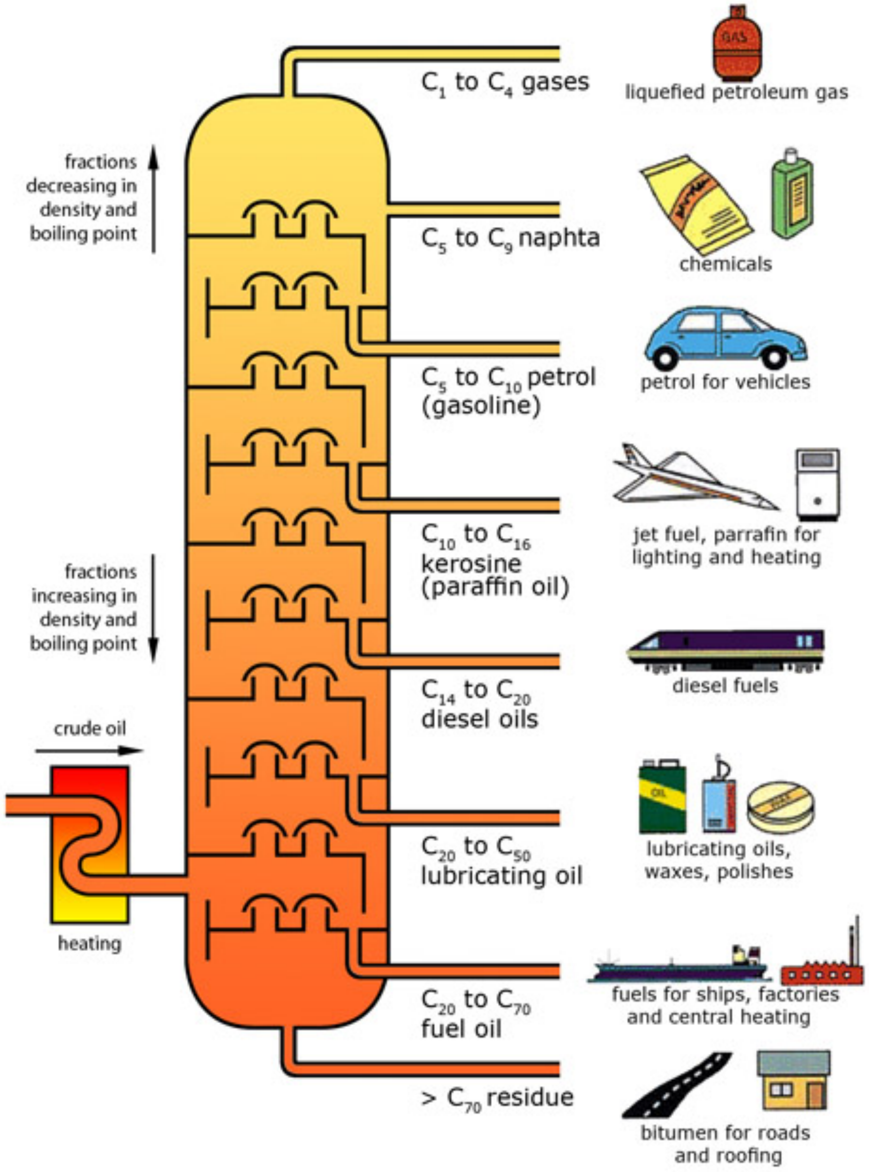
www.theguardian.com

Global Consumption of Crude Oil is Increasing Rapidly



Source: Deutsche Bank

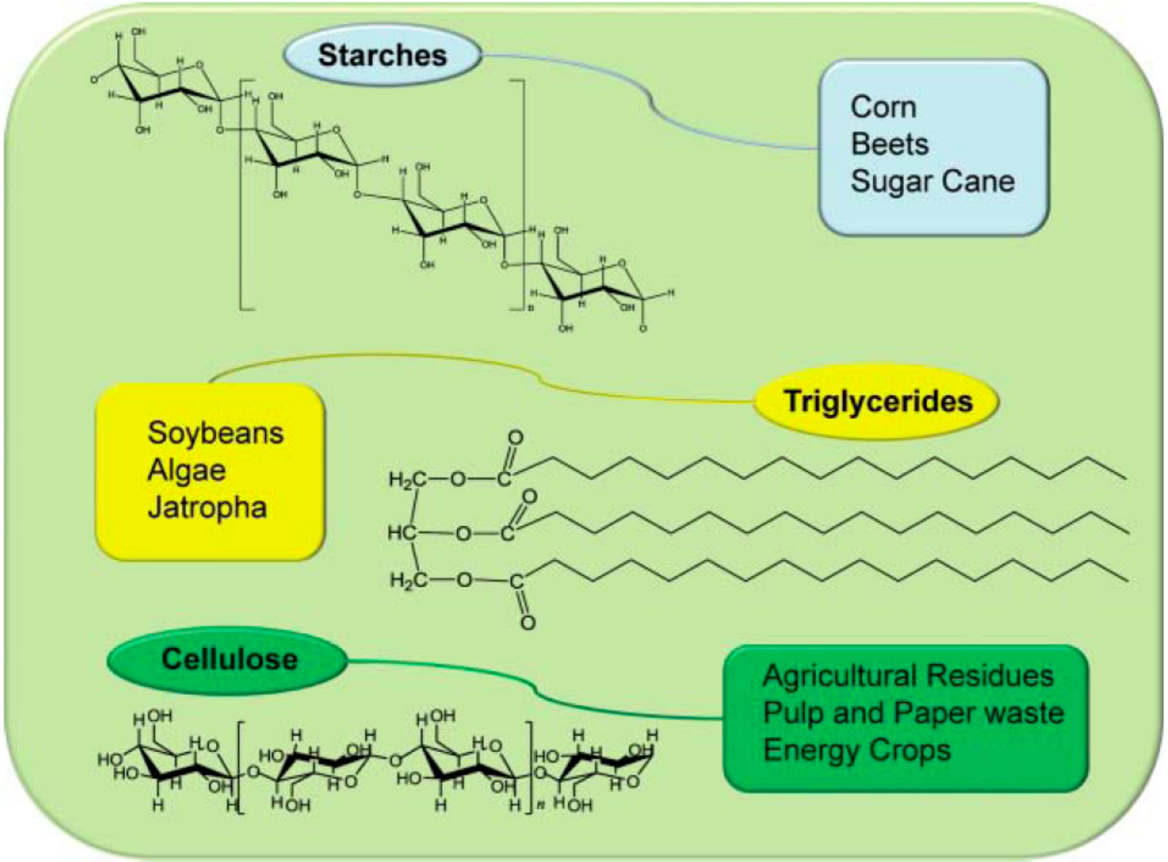
Fractional Distillation Separates Crude Oil into Various Applications



Convention Methods for Obtaining Hydrocarbon Fuel

Can we devise strategies to synthesize high energy density hydrocarbons from renewable and abundant feedstocks that take advantage of already established infrastructure?

Three Major Biomass Sources



Starches

Corn
Beets
Sugar Cane

Triglycerides

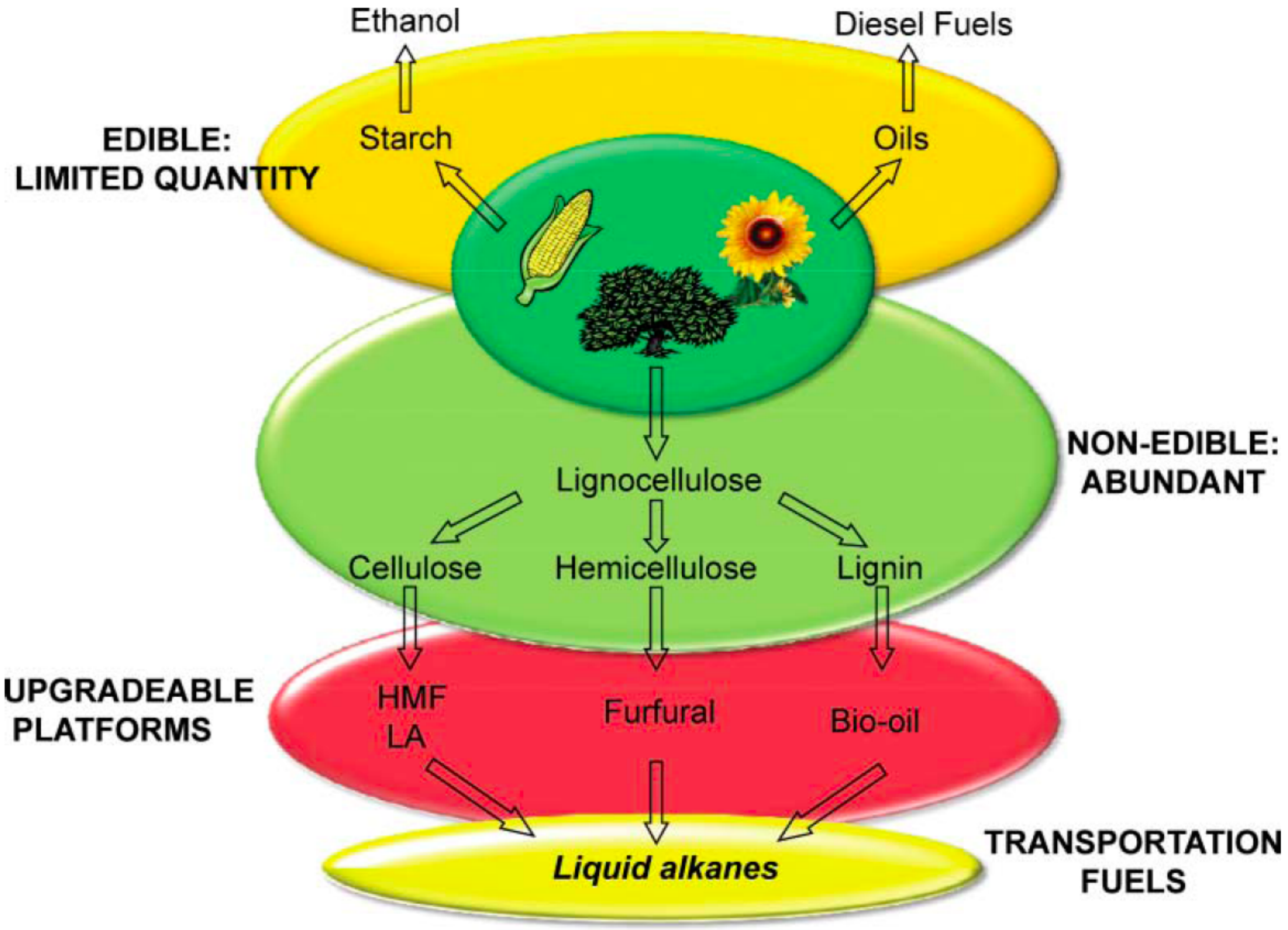
Soybeans
Algae
Jatropha

Cellulose

Agricultural Residues
Pulp and Paper waste
Energy Crops

Alonso, D. M.; Bond, J. Q.; Dumesic, J. A. *Green Chem.* **2010**, *12*, 1493.

Typical Biomass Degradation Pathways

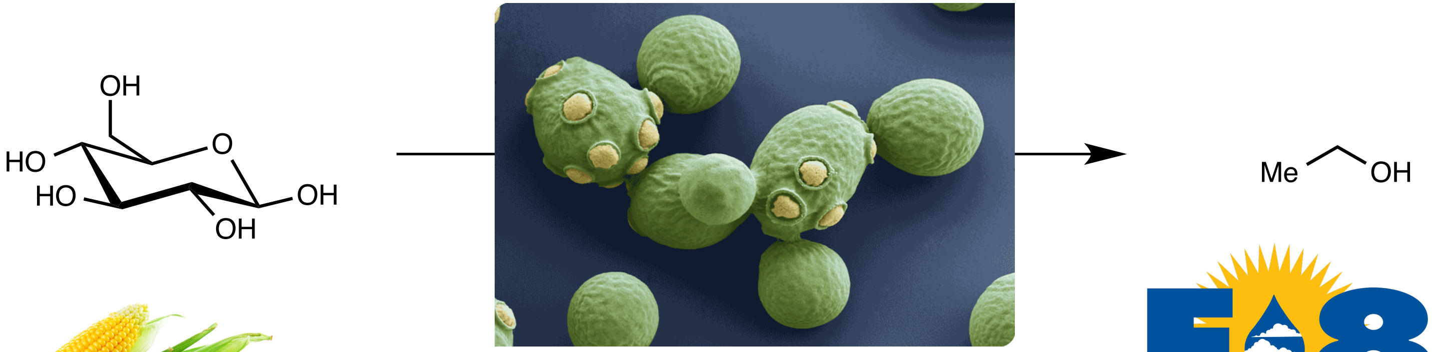


Alonso, D. M.; Bond, J. Q.; Dumesic, J. A. *Green Chem.* **2010**, *12*, 1493.

Bioethanol Produced via Fermentation Pathway

Starch

Sugar



Saccharomyces cerevisiae

E85
85% Ethanol

FLEX FUEL

Global production of bioethanol via fermentation processes = 110 billion L in 2011

Bioethanol can be used as 5-10% additive in conventional gasoline

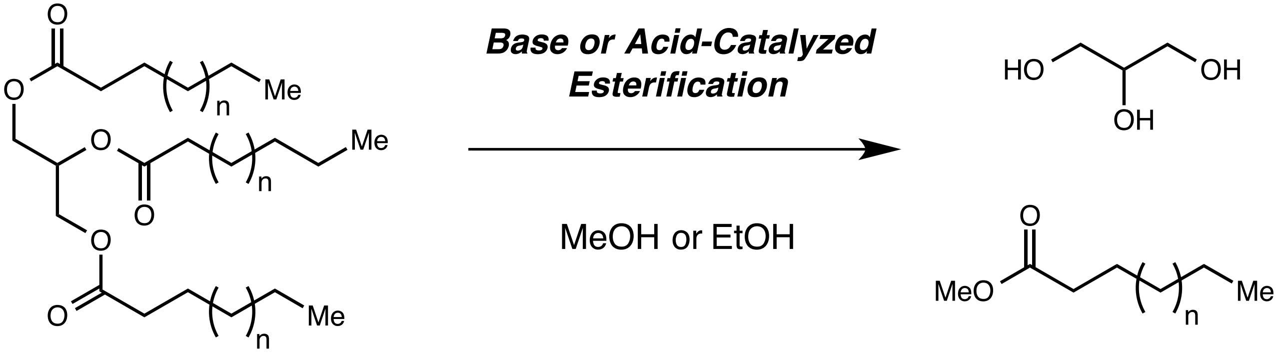
85% bioethanol can be used in E85 FFV (flexible fuel vehicles)

Alonso, D. M.; Bond, J. Q.; Dumesic, J. A. *Green Chem.* **2010**, *12*, 1493.

Biodiesel Produced via Esterification of Lipids

Triglycerides

Lipids



Base or Acid-Catalyzed Esterification

MeOH or EtOH

Glycerol

"Biodiesel"

US production of biodiesel in 2013 = 1.8 billion gallons

Common sources of biodiesel = soybean oil (accounts for 1/2 of US production), rapeseed, jatropha

Biodiesel can be used alone or blended with petrodiesel

www.biodiesel.org/production/production-statistics

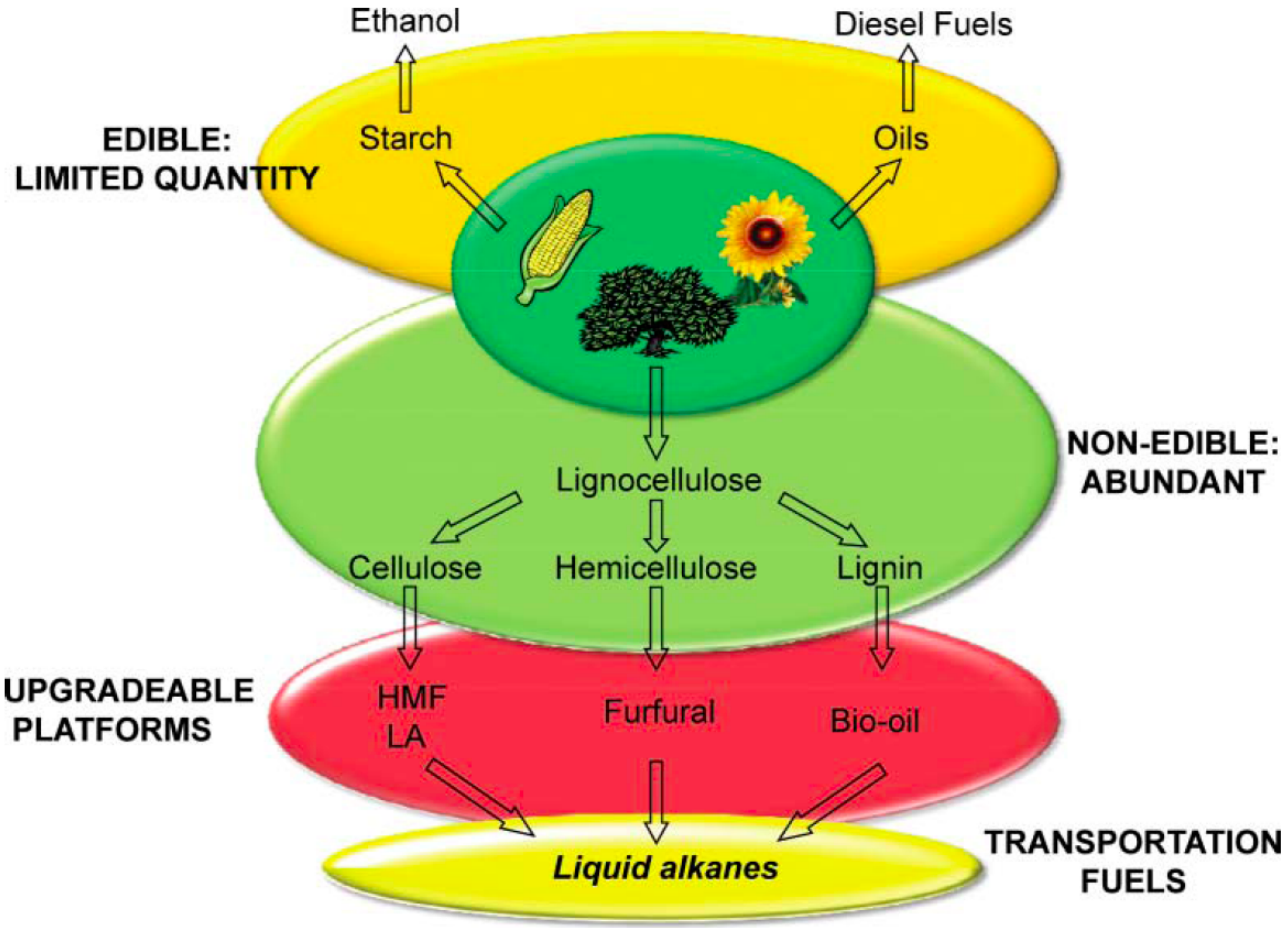
Alonso, D. M.; Bond, J. Q.; Dumesic, J. A. *Green Chem.* **2010**, *12*, 1493.

Drawbacks to Bioethanol and Biodiesel

Despite helping to supplement petrochemicals, bioethanol and biodiesel consume edible feedstocks...

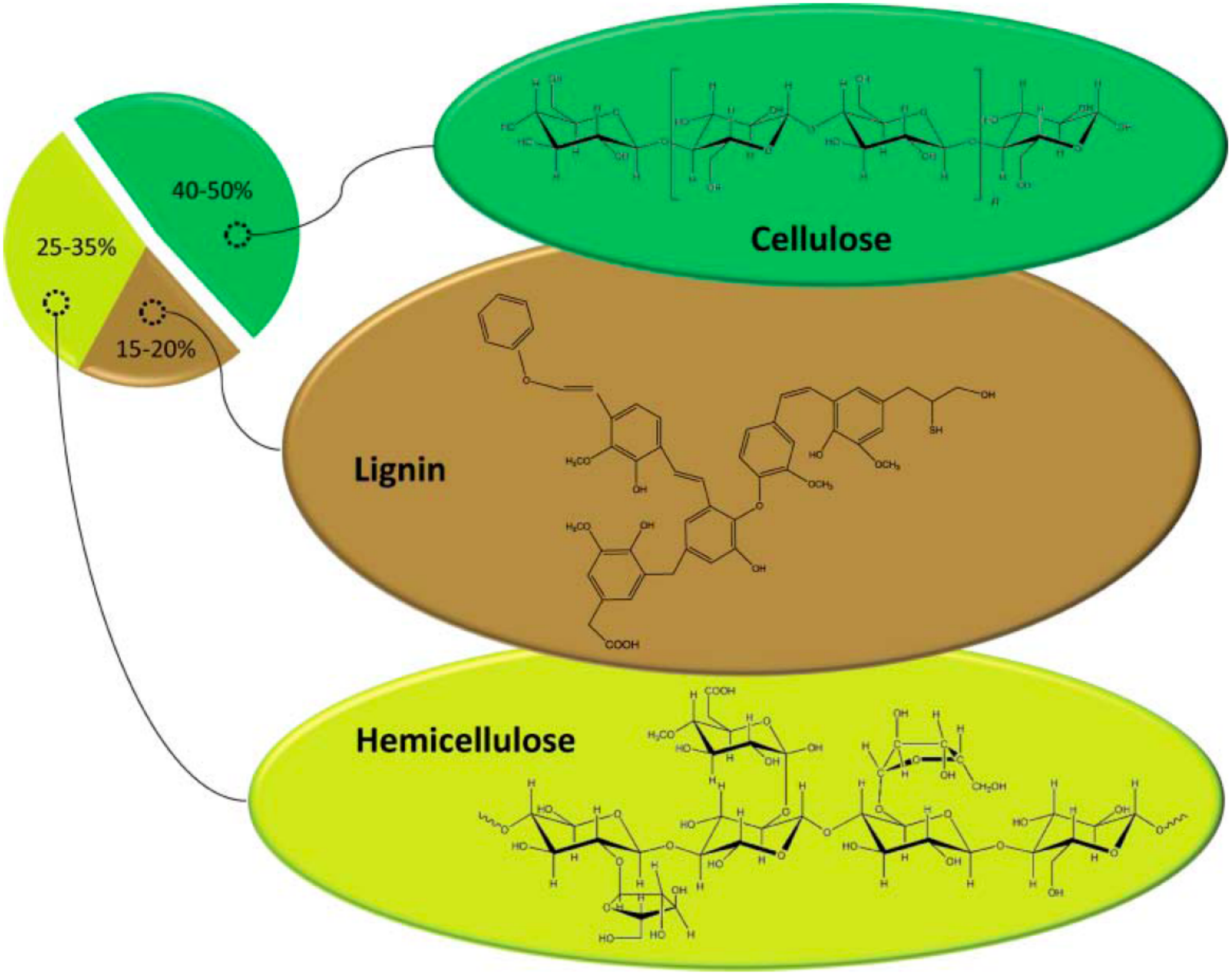
Can we use the non-edible, "waste" segment of biomass to produce biofuels?

Typical Biomass Degradation Pathways



Alonso, D. M.; Bond, J. Q.; Dumesic, J. A. *Green Chem.* **2010**, *12*, 1493.

Three Major Components of Lignocellulose



Alonso, D. M.; Bond, J. Q.; Dumesic, J. A. *Green Chem.* **2010**, *12*, 1493.

Fundamentals of Biomass Conversion to Biofuels

- Considering the composition of biomass vs. biofuels, two major challenges:

1) Reducing high oxygen content of biomass feedstock to increase energy density

2) Forming C–C bonds between monomers to form hydrocarbons with appropriate volatility and molecular weight for use as transportation fuels

- General strategy in the field comprises two major steps:

1) Degrading lignocellulosic feedstock to gaseous/liquid "platform chemical" (via partial removal of oxygen content)

2) Catalytic upgrading of platform chemical to hydrocarbon fuel (via C–C coupling reactions and removal of remaining oxygen functionality)

Tuck, C. O.; Perez, E.; Horvath, I. T.; Sheldon, R. A.; Poliakoff, M. *Science* **2012**, *337*, 695.

Alonso, D. M.; Bond, J. Q.; Dumesic, J. A. *Green Chem.* **2010**, *12*, 1493.

Thermochemical Methods for Biomass Degradation

■ Three main methods of themal processing of biomass:

Gasification

- Combustion of biomass to produce syngas (CO/H_2) at temperatures >1000 K
- Syngas can be upgraded via Fischer-Tropsch synthesis

Pyrolysis

- Thermal anaerobic decomposition (650-800 K) then cooling produce liquid mixture of ~350 products (acids, aldehydes, ketones, esters, aromatics) referred to as "bio-oil"
- Bio-oil is amenable to upgrading strategies but still has high oxygen content

Liquefaction

- Thermal decomposition (525-725 K) in the presence of water and basic catalysts (eg. Na_2CO_3) at high pressures (5-20 atm)
- Bio-oil product contains less 12-14% less oxygen than pyrolysis

■ Aqueous-Phase Reforming

- Low temperature (~500 K) method for converting biomass into H_2 stream (with CO_2 byproduct)
- Dehydrogenation over Pt catalyst, followed by C–C/C–O bond cleavage

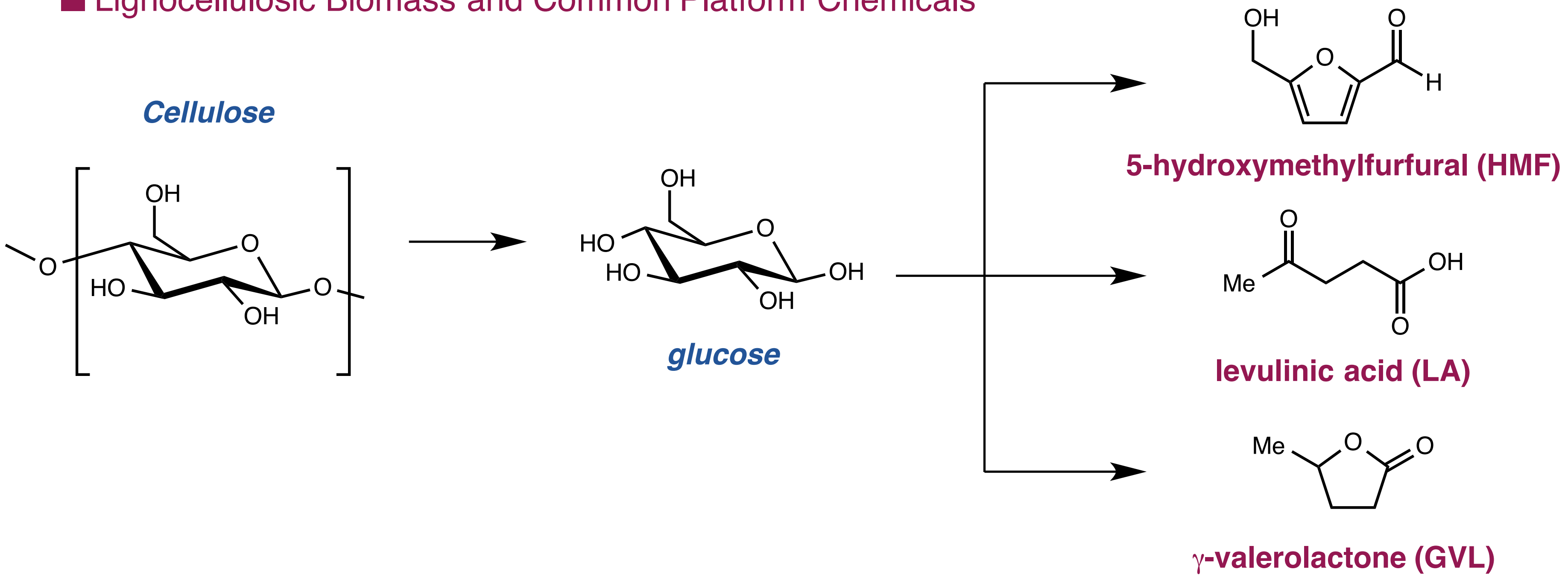
Cortright, R. D.; Davda, R. R.; Dumesic, J. A. *Nature* **2002**, *418*, 964.

Kunkes, E. L.; Simonetti, D. A.; West, R. M.; Serrano-Ruiz, J. C.; Gartner, C. A.; Dumesic, J. A. *Science* **2008**, *322*, 417.

Alonso, D. M.; Bond, J. Q.; Dumesic, J. A. *Green Chem.* **2010**, *12*, 1493.

Important Platform Chemicals from Lignocellulosic Biomass

■ Lignocellulosic Biomass and Common Platform Chemicals



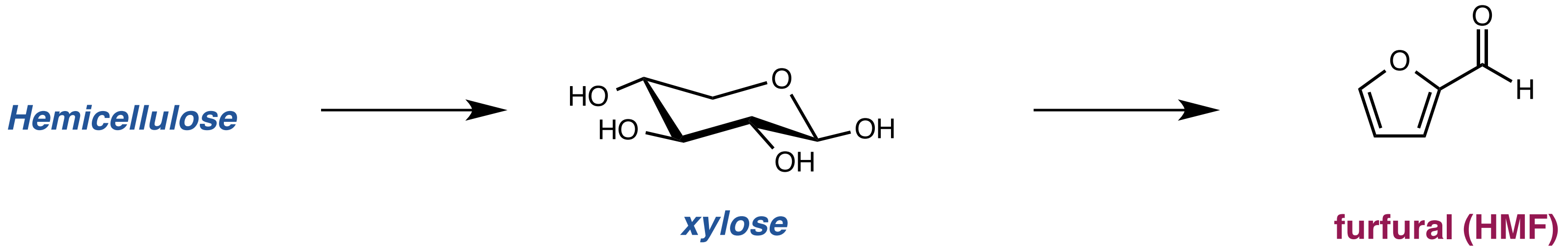
Cellulose

glucose

5-hydroxymethylfurfural (HMF)

levulinic acid (LA)

γ-valerolactone (GVL)



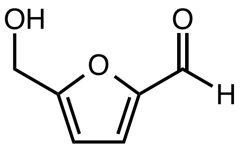
Hemicellulose

xylose

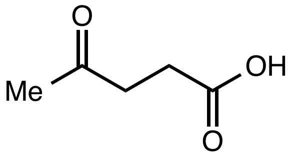
furfural (HMF)

Alonso, D. M.; Bond, J. Q.; Dumesic, J. A. *Green Chem.* **2010**, *12*, 1493.

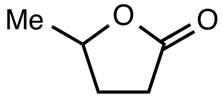
Platform Chemicals and Upgrading Strategies



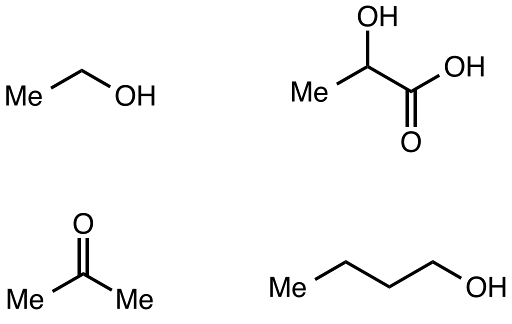
5-hydroxymethylfurfural (HMF)



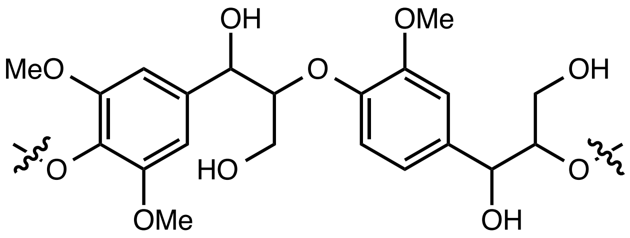
levulinic acid (LA)



γ-valerolactone (GVL)

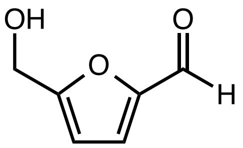


fermentation products

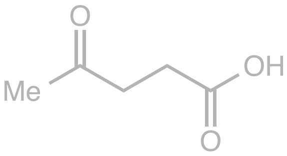


lignin

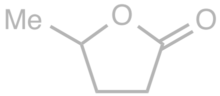
Platform Chemicals and Upgrading Strategies



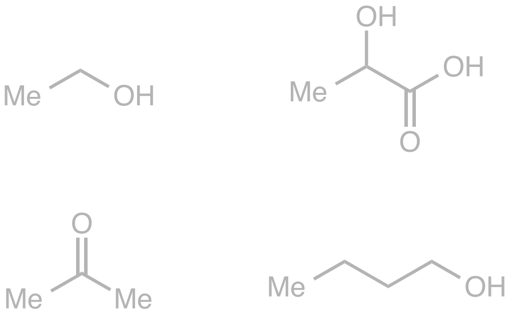
5-hydroxymethylfurfural (HMF)



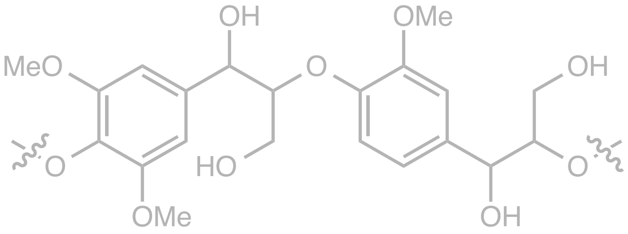
levulinic acid (LA)



γ-valerolactone (GVL)



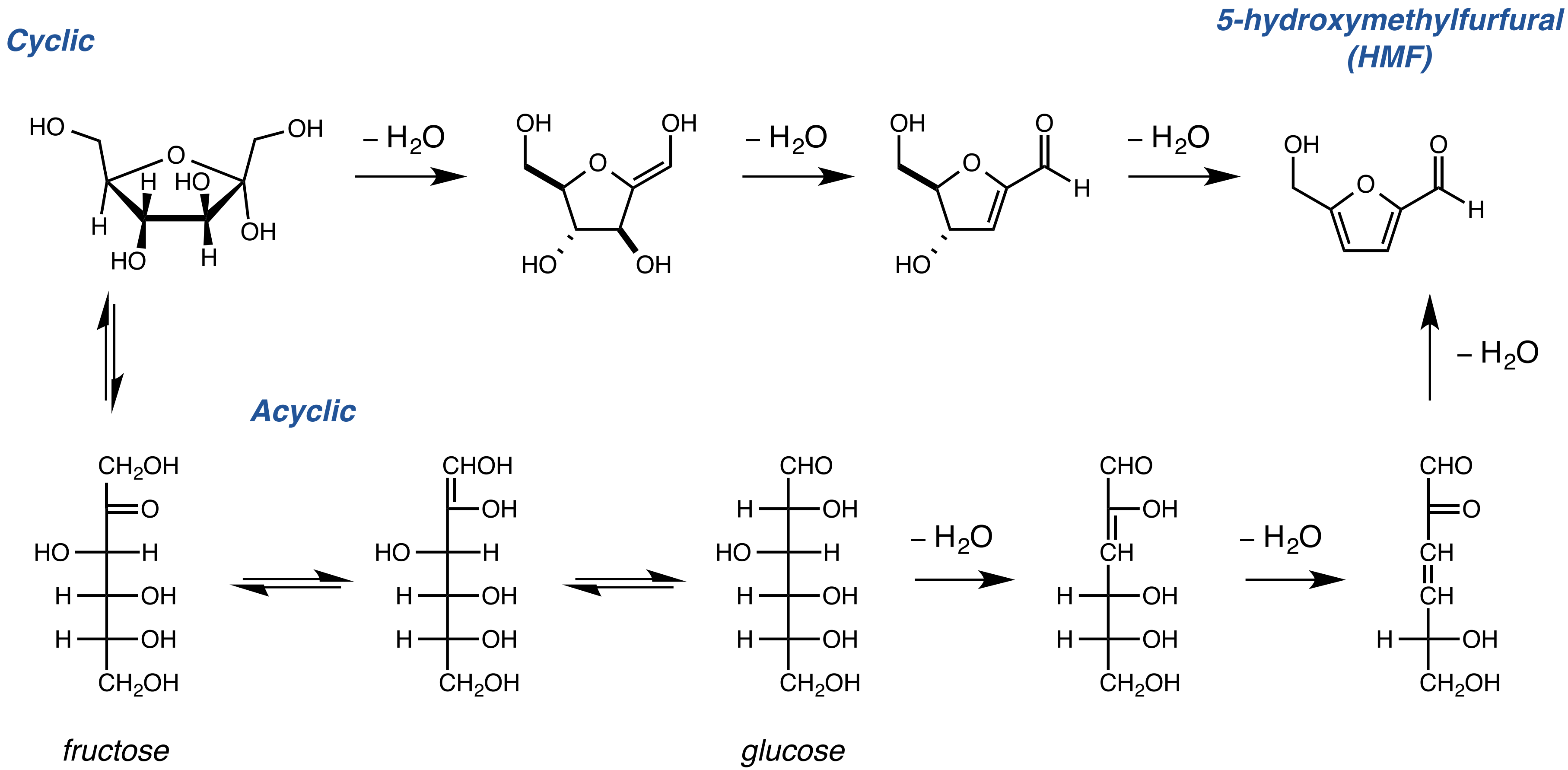
fermentation products



lignin

Acid-Catalyzed Dehydration of Hexoses to HMF

- Two mechanisms have been proposed for dehydration of hexoses



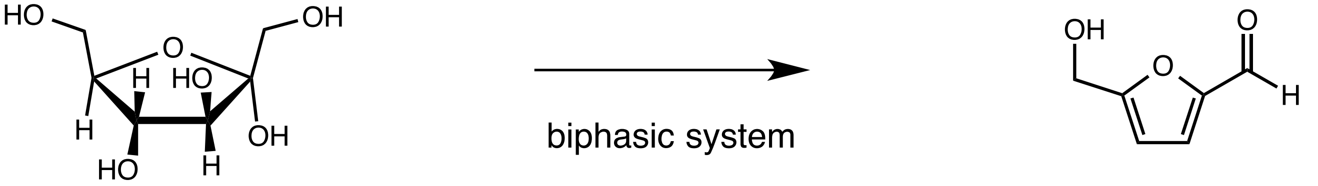
fructose

glucose

Corma, A.; Iborra, S.; Velty, A. *Chem. Rev.* **2007**, *107*, 2411.

Dumesic's Synthesis of HMF from Fructose

- Dumesic develops biphasic system for efficient HMF synthesis from fructose



Fructose

5-hydroxymethylfurfural

~80% yield

Feedstock sugar

Readily accessible via isomerization of glucose

Glucose is product of cellulose degradation

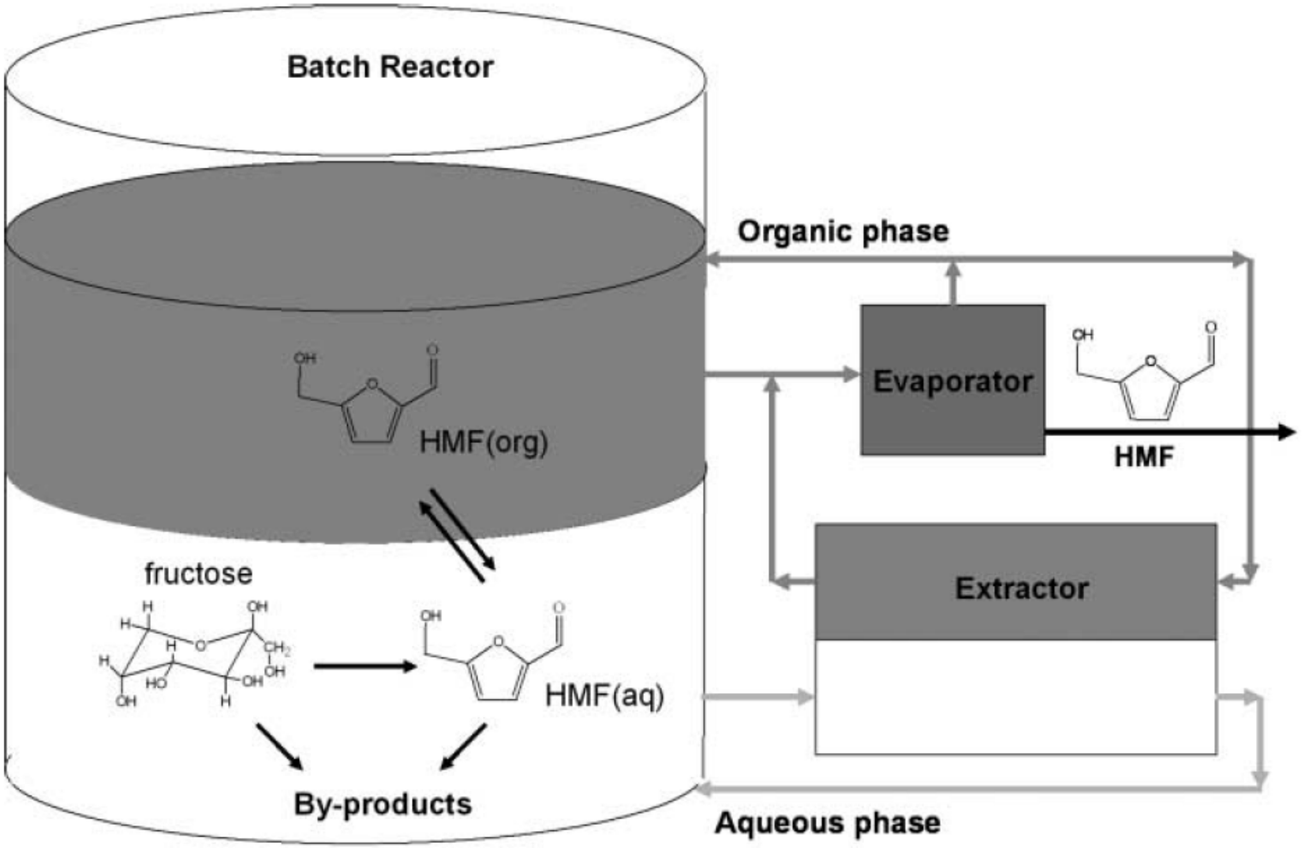
Platform chemical

Upgradable to alkanes

Roman-Leshkov, Y.; Chheda, J. N.; Dumesic, J. A. *Science* **2006**, *312*, 1933.

Dumesic's Synthesis of HMF from Fructose

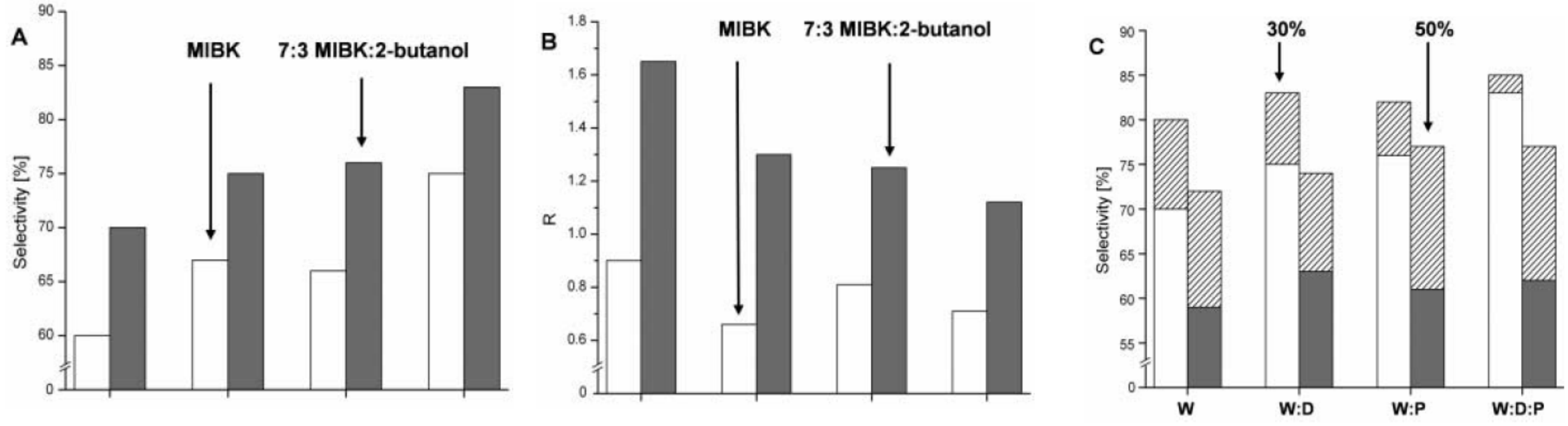
- Dumesic develops biphasic system for efficient HMF synthesis from fructose



Roman-Leshkov, Y.; Chheda, J. N.; Dumesic, J. A. *Science* **2006**, *312*, 1933.

Dumesic's Synthesis of HMF from Fructose

- Both HMF yield and extraction ratio (R) increase with addition of 2-butanol
- Lower concentration of fructose increases HMF yield
  - Hashed bars indicate double volume of organic phase



Aqueous phase:

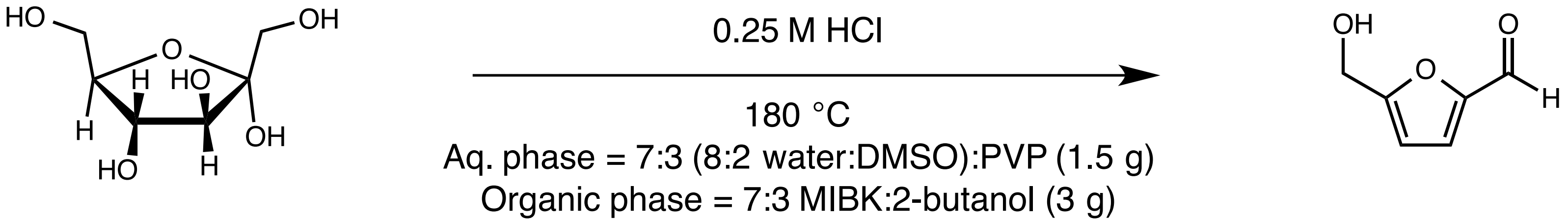
W = water
W:D = 8:2 water:DMSO
W:P = 7:3 water:PVP
W:D:P = 7:3 (8:2 water:DMSO):PVP

$$R = \frac{[\mathrm{HMF}]_{org}}{[\mathrm{HMF}]_{aq}}$$

Roman-Leshkov, Y.; Chheda, J. N.; Dumesic, J. A. *Science* **2006**, *312*, 1933.

Dumesic's Synthesis of HMF from Fructose

- Dumesic develops biphasic system for efficient HMF synthesis from fructose



0.25 M HCl

180 °C
Aq. phase = 7:3 (8:2 water:DMSO):PVP (1.5 g)
Organic phase = 7:3 MIBK:2-butanol (3 g)

30 wt % fructose

5-hydroxymethylfurfural

85% yield
89% conversion

Dumesic system minimizes undesired byproducts

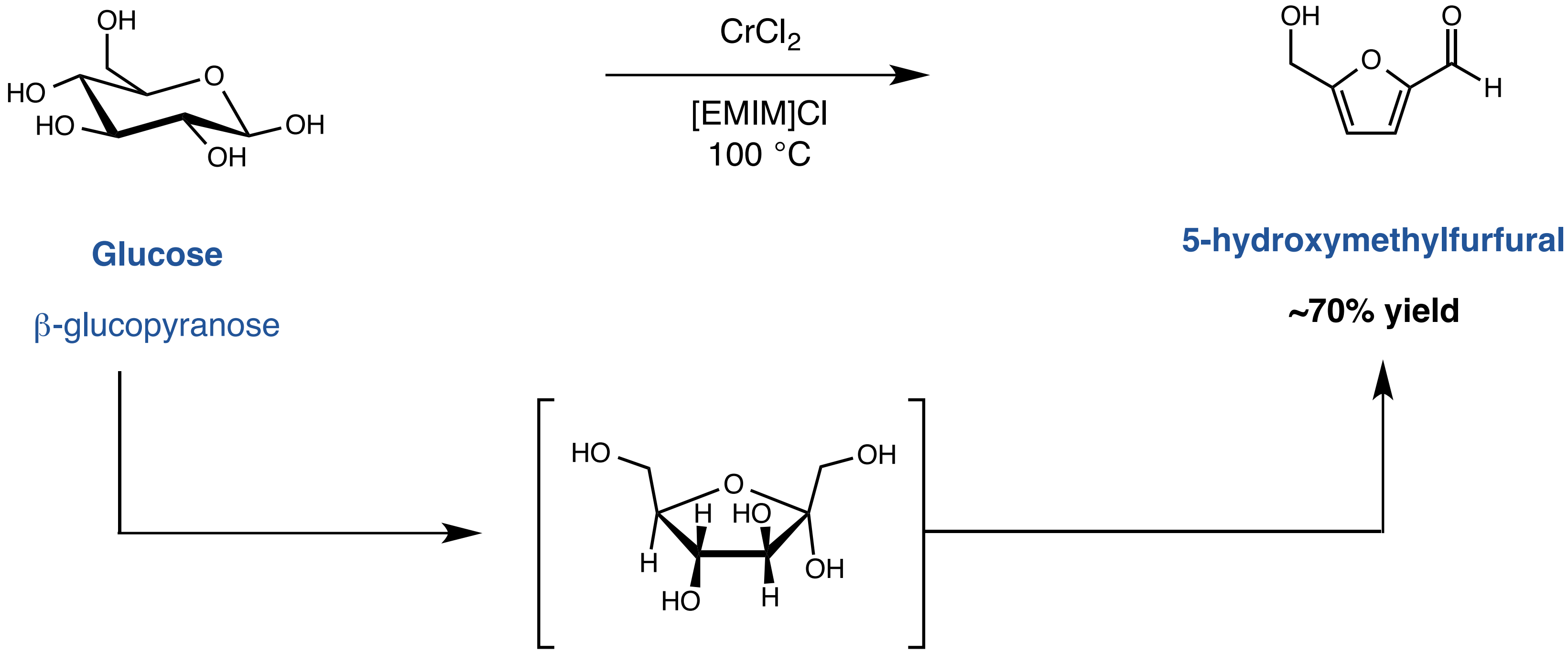
Organic phase enables easy isolation and purification of HMF product for future upgrading

Limited to fructose (additional synthetic step from glucose)

Roman-Leshkov, Y.; Chheda, J. N.; Dumesic, J. A. *Science* **2006**, *312*, 1933.

Zhang's Synthesis of HMF from Glucose

- Zhang develops expedient route to HMF from glucose using ionic liquids and metal chlorides
  - Zhang discovers a route to take glucose directly to HMF
  - Chromium salts are necessary catalyst



Glucose

β-glucopyranose

5-hydroxymethylfurfural

~70% yield

Fructose

Zhao, H.; Holladay, J. E.; Brown, H.; Zhang, Z. C. *Science* **2007**, *316*, 1597.

Zhang's Synthesis of HMF from Glucose

- Zhang observes HMF formation from fructose but not glucose in presence of [EMIM]Cl

  - [EMIM]Cl = 1-ethyl-3-methylimidazolium chloride

  - [EMIM]Cl serves as both solvent and acid catalyst

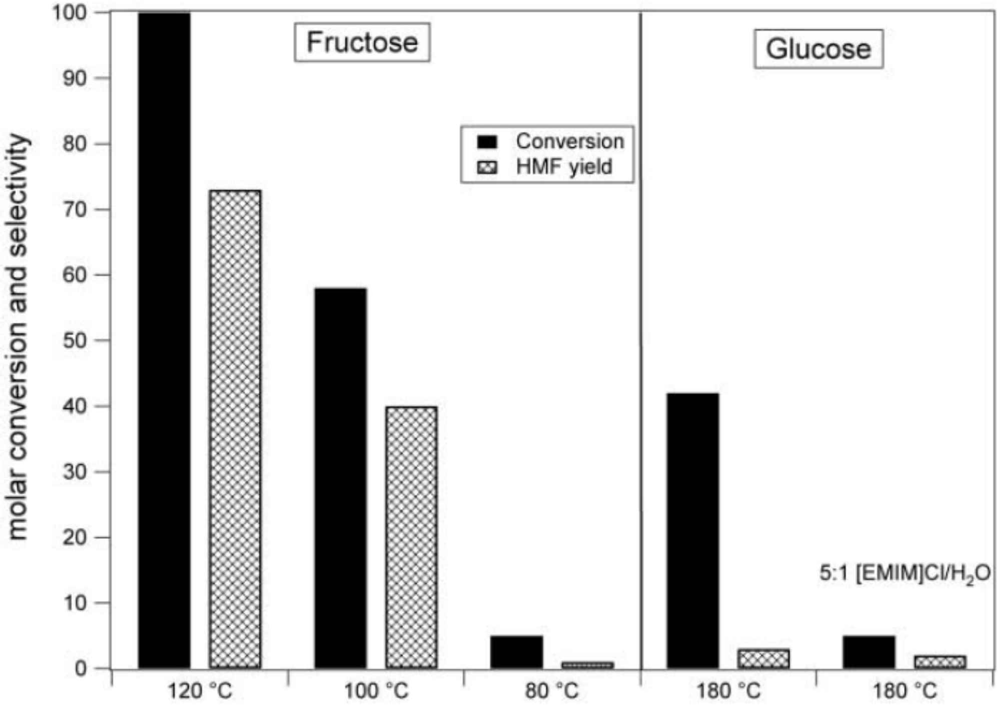
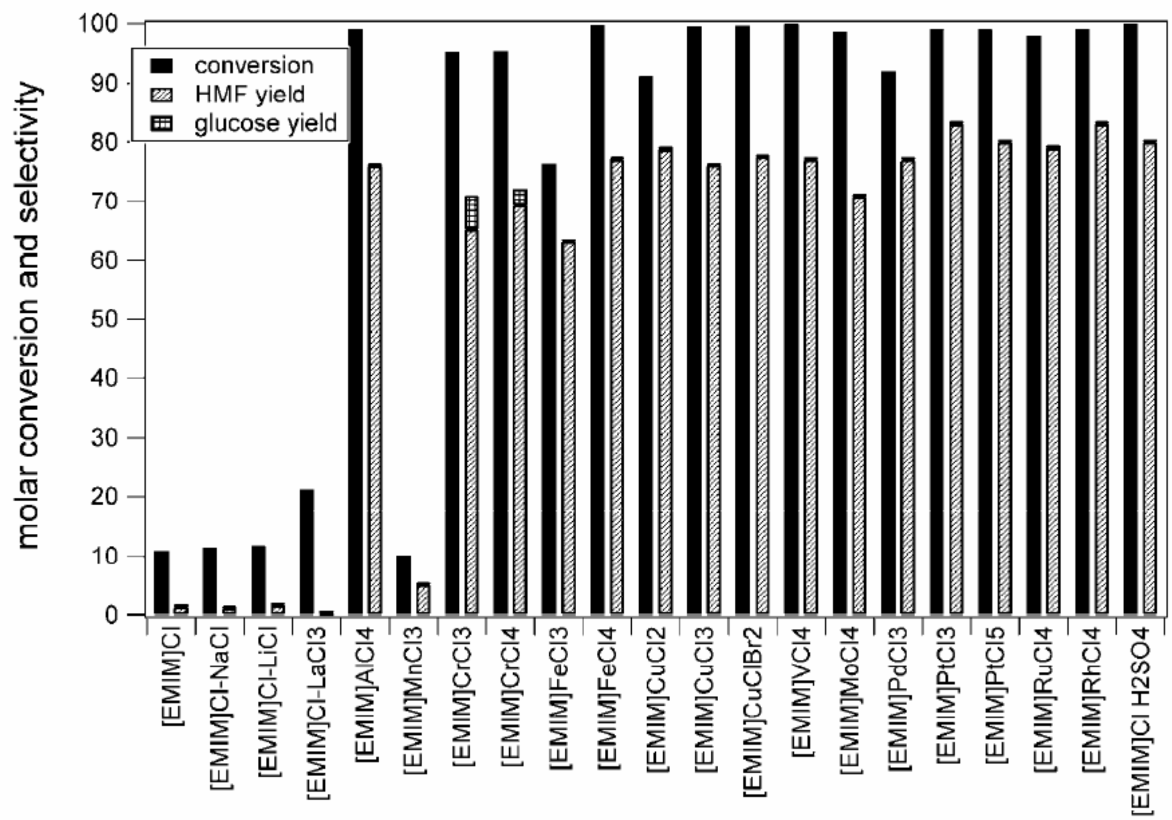


Fig. 2. Fructose and glucose conversion in [EMIM]Cl. Fifty mg of sugar was added to 500 mg of [EMIM]Cl and heated for 3 hours at the temperature indicated (no catalyst was added).

Zhao, H.; Holladay, J. E.; Brown, H.; Zhang, Z. C. *Science* **2007**, *316*, 1597.

Zhang's Synthesis of HMF from Glucose

- HMF is formed from fructose at 80 °C in presence of catalytic metal halides
  - 6 mol% metal halide, 3 hour reaction time
  - H_2SO_4 was also effective at 18 mol% (80% yield) and 1.8 mol% (75% yield)



Zhao, H.; Holladay, J. E.; Brown, H.; Zhang, Z. C. *Science* **2007**, *316*, 1597.

Zhang's Synthesis of HMF from Glucose

- HMF is formed directly from glucose at 100 °C in presence of $CrCl_2$

  - $CrCl_2$ and $CrCl_3$ were the only catalysts that gave appreciable HMF yield (70% with $CrCl_2$)

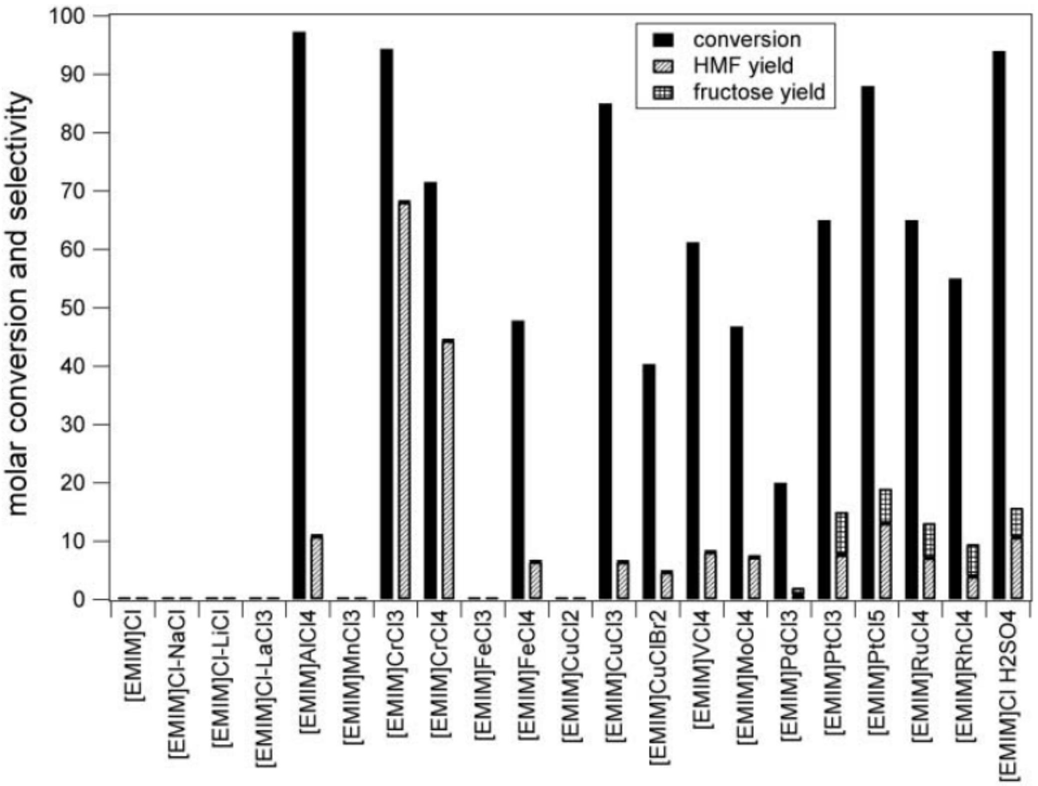


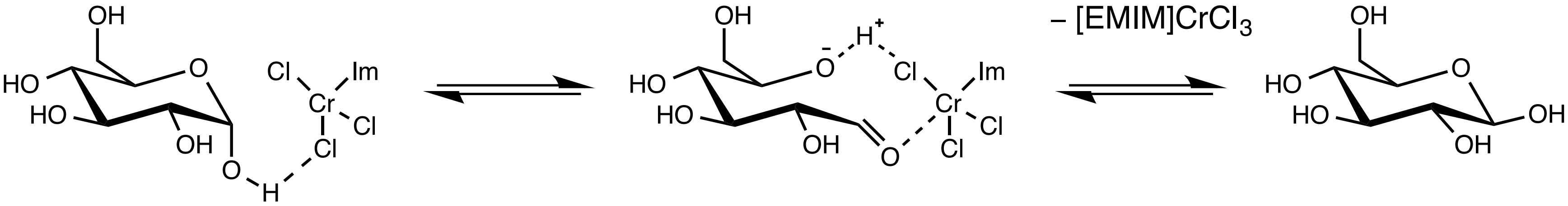
Fig. 3. Glucose conversion in [EMIM]Cl treated with numerous catalysts, most of which are effective for fructose dehydration. Only $CrCl_2$ leads to high HMF yield from glucose.

Zhao, H.; Holladay, J. E.; Brown, H.; Zhang, Z. C. *Science* **2007**, *316*, 1597.

Zhang's Synthesis of HMF from Glucose

- CrCl$_2$ presumably enables isomerization of glucose to fructose

- Mutarotation enables α-β interconversion



α-glucopyranose

β-glucopyranose

- Mutarotation does not occur in the presence of [EMIM]Cl

- Equilibrium mixture of α and β anomers generated in presence of catalytic CrCl$_2$ or CuCl$_2$

- Sugar-metal coordination is implied in mechanism

Zhao, H.; Holladay, J. E.; Brown, H.; Zhang, Z. C. *Science* **2007**, *316*, 1597.

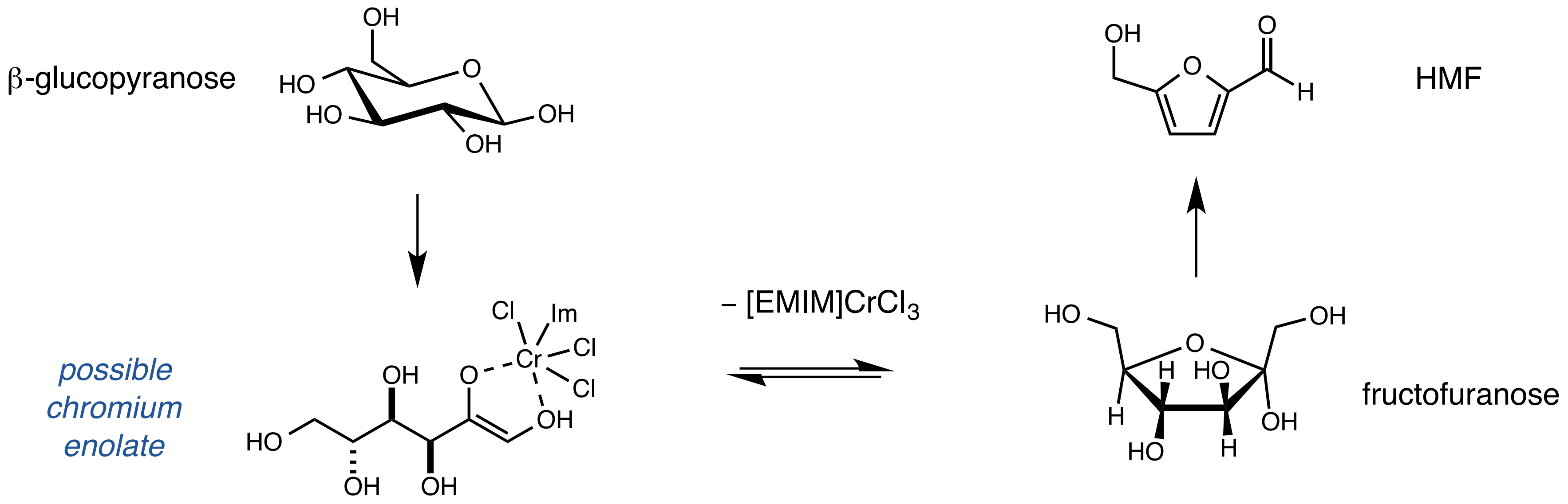
Zhang's Synthesis of HMF from Glucose

■ $CrCl_2$ presumably enables isomerization of glucose to fructose

- Series of control and competition experiments support sugar-metal coordination

Additive:	Glycerol	Glyceraldehyde	bipyridine
HMF Yield:	70%	<20%	<2%

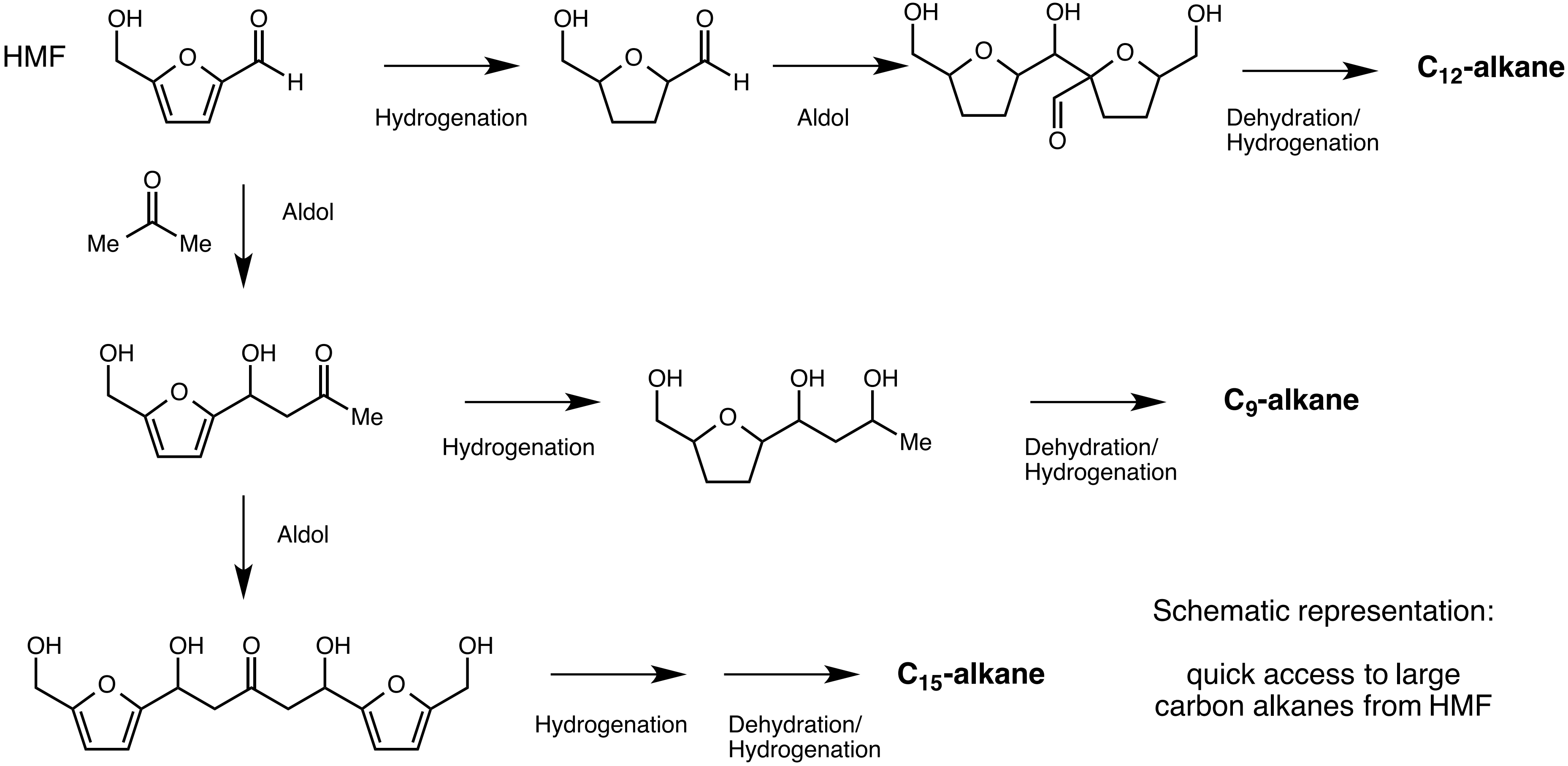
■ Proposed mechanism



Zhao, H.; Holladay, J. E.; Brown, H.; Zhang, Z. C. *Science* **2007**, *316*, 1597.

Dumesic's Aqueous Phase Processing of HMF to Alkanes

- Series of aldol condensations, hydrogenations, and dehydrations convert HMF to alkanes



Schematic representation:

quick access to large
carbon alkanes from HMF

Huber, G. W.; Chheda, J. N.; Barrett, C. J.; Dumesic, J. A. *Science* **2005**, *308*, 1446.

Dumesic's Aqueous Phase Processing of HMF to Alkanes

- Four Phase Dehydration/Hydrogenation (4-PD/H) reactor system

1) Aqueous stream containing organic reactant

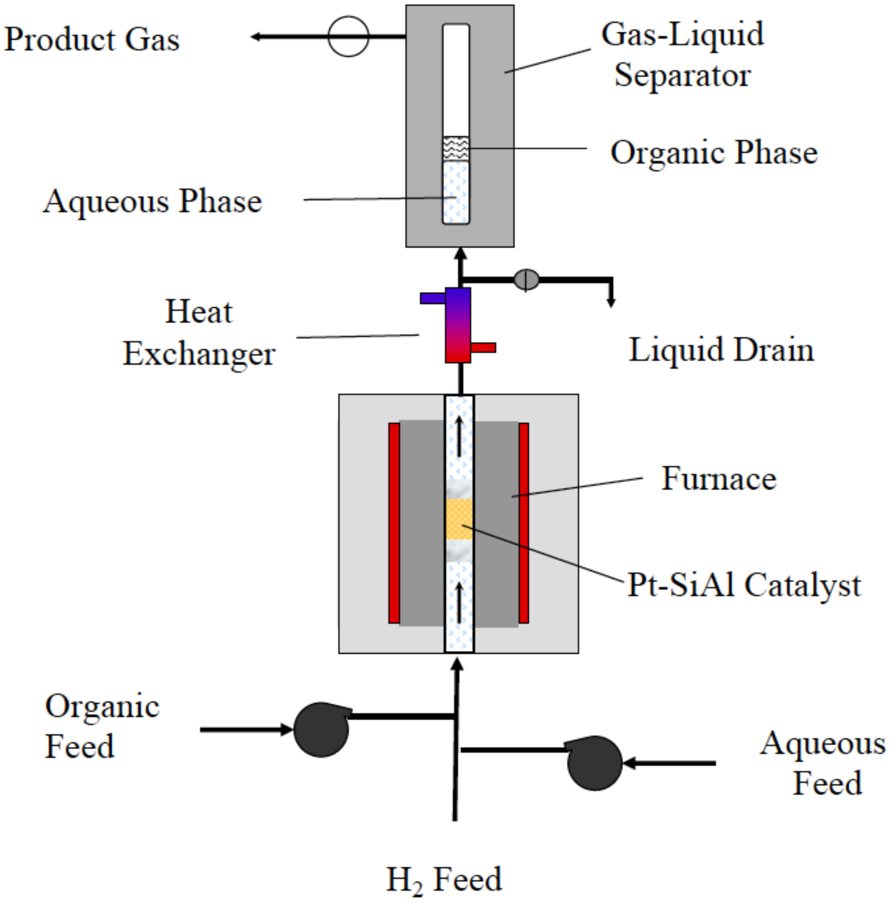
2) Hexadecane organic stream

3) H_2 gas stream

4) Solid Pt/SiO_2-Al_2O_3 catalyst

Conditions:

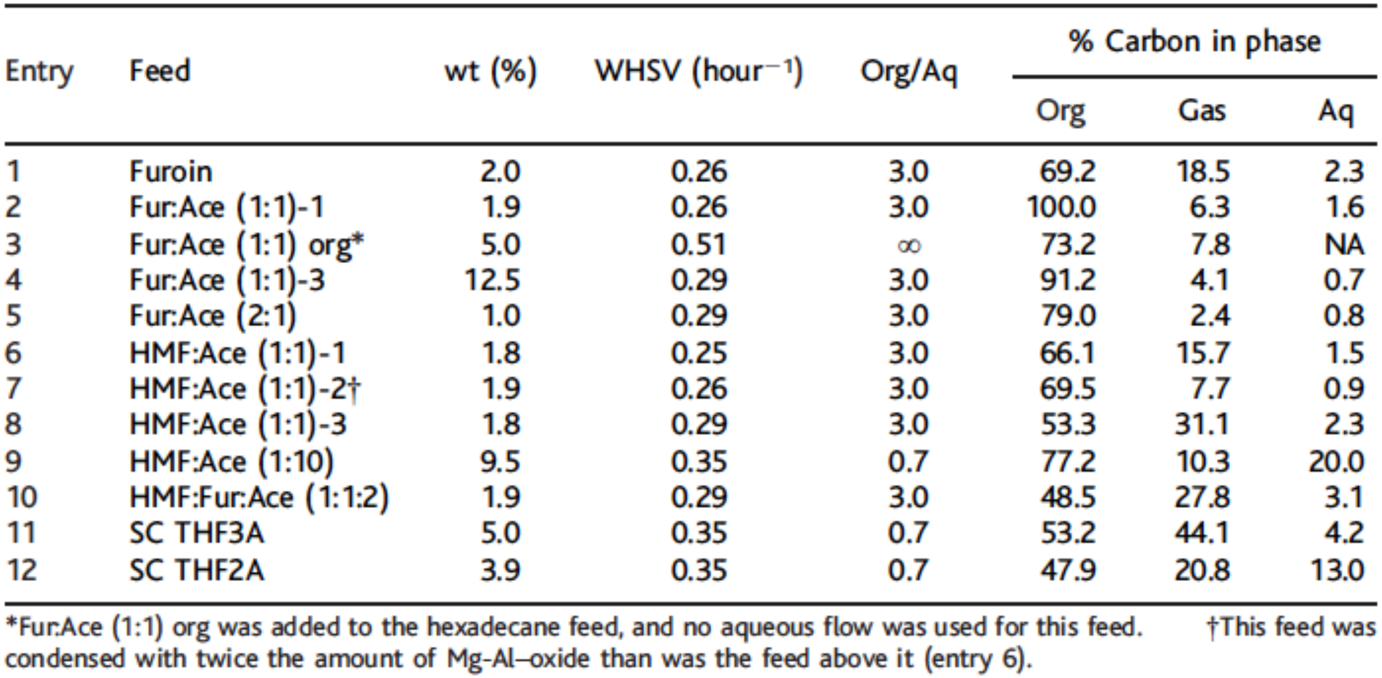
250–265 °C
52–60 bar
4 wt% catalyst



Huber, G. W.; Chheda, J. N.; Barrett, C. J.; Dumesic, J. A. *Science* **2005**, *308*, 1446.

Dumesic's Aqueous Phase Processing of HMF to Alkanes

- Conversion of various biomass-derived feeds in the 4-PD/H reactor



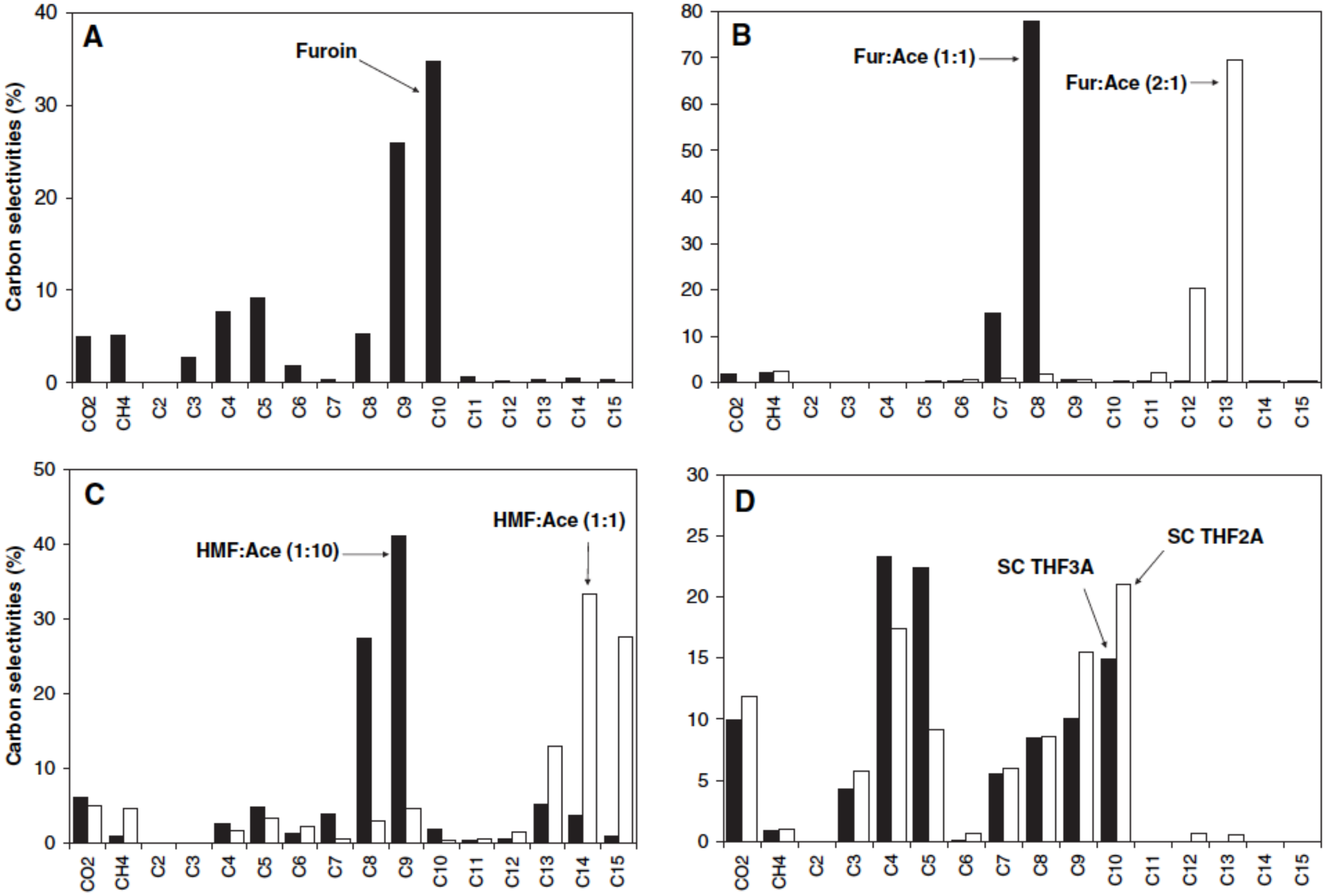
Entry	Feed	wt (%)	WHSV ($hour^{-1}$)	Org/Aq	% Carbon in phase		
					Org	Gas	Aq
1	Furoin	2.0	0.26	3.0	69.2	18.5	2.3
2	Fur:Ace (1:1)-1	1.9	0.26	3.0	100.0	6.3	1.6
3	Fur:Ace (1:1) org*	5.0	0.51	∞	73.2	7.8	NA
4	Fur:Ace (1:1)-3	12.5	0.29	3.0	91.2	4.1	0.7
5	Fur:Ace (2:1)	1.0	0.29	3.0	79.0	2.4	0.8
6	HMF:Ace (1:1)-1	1.8	0.25	3.0	66.1	15.7	1.5
7	HMF:Ace (1:1)-2†	1.9	0.26	3.0	69.5	7.7	0.9
8	HMF:Ace (1:1)-3	1.8	0.29	3.0	53.3	31.1	2.3
9	HMF:Ace (1:10)	9.5	0.35	0.7	77.2	10.3	20.0
10	HMF:Fur:Ace (1:1:2)	1.9	0.29	3.0	48.5	27.8	3.1
11	SC THF3A	5.0	0.35	0.7	53.2	44.1	4.2
12	SC THF2A	3.9	0.35	0.7	47.9	20.8	13.0

*Fur:Ace (1:1) org was added to the hexadecane feed, and no aqueous flow was used for this feed. †This feed was condensed with twice the amount of Mg-Al–oxide than was the feed above it (entry 6).

Huber, G. W.; Chheda, J. N.; Barrett, C. J.; Dumesic, J. A. *Science* **2005**, *308*, 1446.

Dumesic's Aqueous Phase Processing of HMF to Alkanes

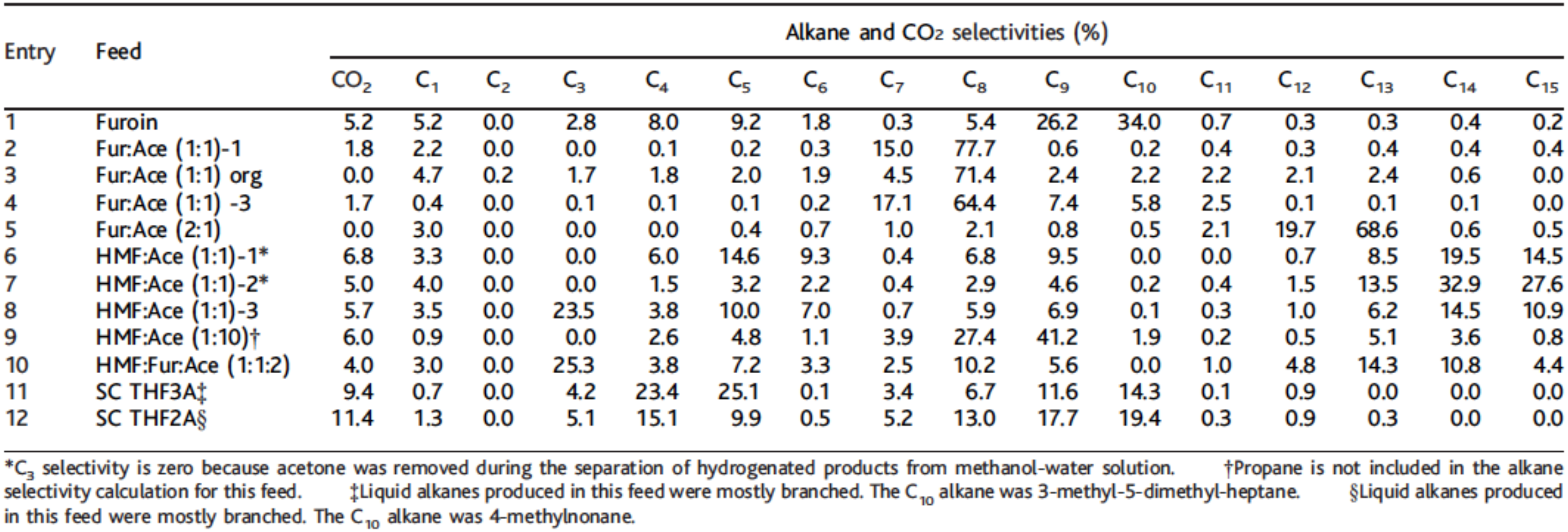
- Carbon selectivities of various biomass-derived feeds in the 4-PD/H reactor



Huber, G. W.; Chheda, J. N.; Barrett, C. J.; Dumesic, J. A. *Science* **2005**, *308*, 1446.

Dumesic's Aqueous Phase Processing of HMF to Alkanes

- Alkane and CO_2 selectivities of various biomass-derived feeds in the 4-PD/H reactor



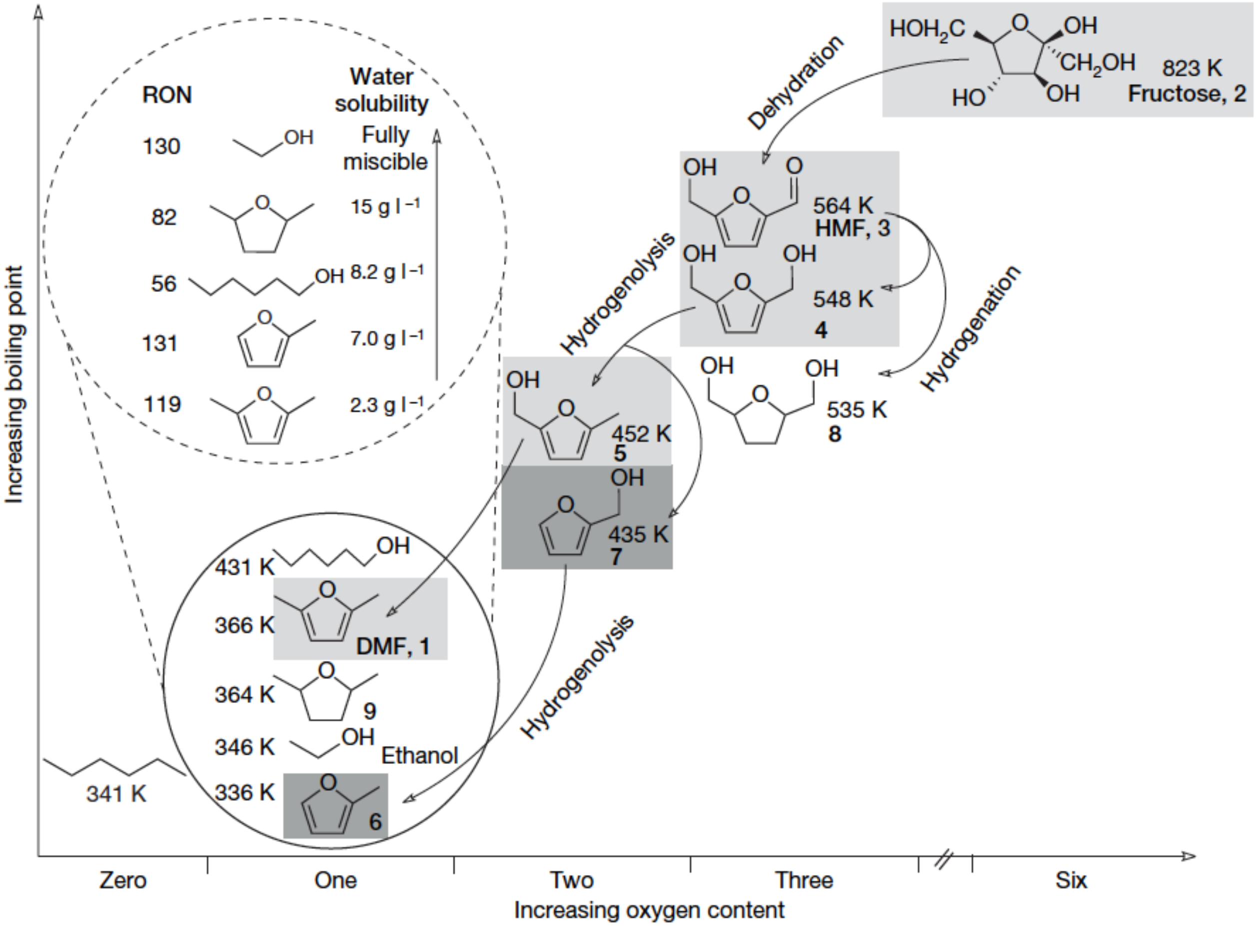
Entry	Feed	Alkane and CO_2 selectivities (%)															
		CO_2	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}
1	Furoin	5.2	5.2	0.0	2.8	8.0	9.2	1.8	0.3	5.4	26.2	34.0	0.7	0.3	0.3	0.4	0.2
2	Fur:Ace (1:1)-1	1.8	2.2	0.0	0.0	0.1	0.2	0.3	15.0	77.7	0.6	0.2	0.4	0.3	0.4	0.4	0.4
3	Fur:Ace (1:1) org	0.0	4.7	0.2	1.7	1.8	2.0	1.9	4.5	71.4	2.4	2.2	2.2	2.1	2.4	0.6	0.0
4	Fur:Ace (1:1) -3	1.7	0.4	0.0	0.1	0.1	0.1	0.2	17.1	64.4	7.4	5.8	2.5	0.1	0.1	0.1	0.0
5	Fur:Ace (2:1)	0.0	3.0	0.0	0.0	0.0	0.4	0.7	1.0	2.1	0.8	0.5	2.1	19.7	68.6	0.6	0.5
6	HMF:Ace (1:1)-1*	6.8	3.3	0.0	0.0	6.0	14.6	9.3	0.4	6.8	9.5	0.0	0.0	0.7	8.5	19.5	14.5
7	HMF:Ace (1:1)-2*	5.0	4.0	0.0	0.0	1.5	3.2	2.2	0.4	2.9	4.6	0.2	0.4	1.5	13.5	32.9	27.6
8	HMF:Ace (1:1)-3	5.7	3.5	0.0	23.5	3.8	10.0	7.0	0.7	5.9	6.9	0.1	0.3	1.0	6.2	14.5	10.9
9	HMF:Ace (1:10)†	6.0	0.9	0.0	0.0	2.6	4.8	1.1	3.9	27.4	41.2	1.9	0.2	0.5	5.1	3.6	0.8
10	HMF:Fur:Ace (1:1:2)	4.0	3.0	0.0	25.3	3.8	7.2	3.3	2.5	10.2	5.6	0.0	1.0	4.8	14.3	10.8	4.4
11	SC THF3A‡	9.4	0.7	0.0	4.2	23.4	25.1	0.1	3.4	6.7	11.6	14.3	0.1	0.9	0.0	0.0	0.0
12	SC THF2A§	11.4	1.3	0.0	5.1	15.1	9.9	0.5	5.2	13.0	17.7	19.4	0.3	0.9	0.3	0.0	0.0

*C_3 selectivity is zero because acetone was removed during the separation of hydrogenated products from methanol-water solution. †Propane is not included in the alkane selectivity calculation for this feed. ‡Liquid alkanes produced in this feed were mostly branched. The C_{10} alkane was 3-methyl-5-dimethyl-heptane. §Liquid alkanes produced in this feed were mostly branched. The C_{10} alkane was 4-methylnonane.

Huber, G. W.; Chheda, J. N.; Barrett, C. J.; Dumesic, J. A. *Science* **2005**, *308*, 1446.

Dumesic's Integrated Method Converting Fructose to Dimethylfuran

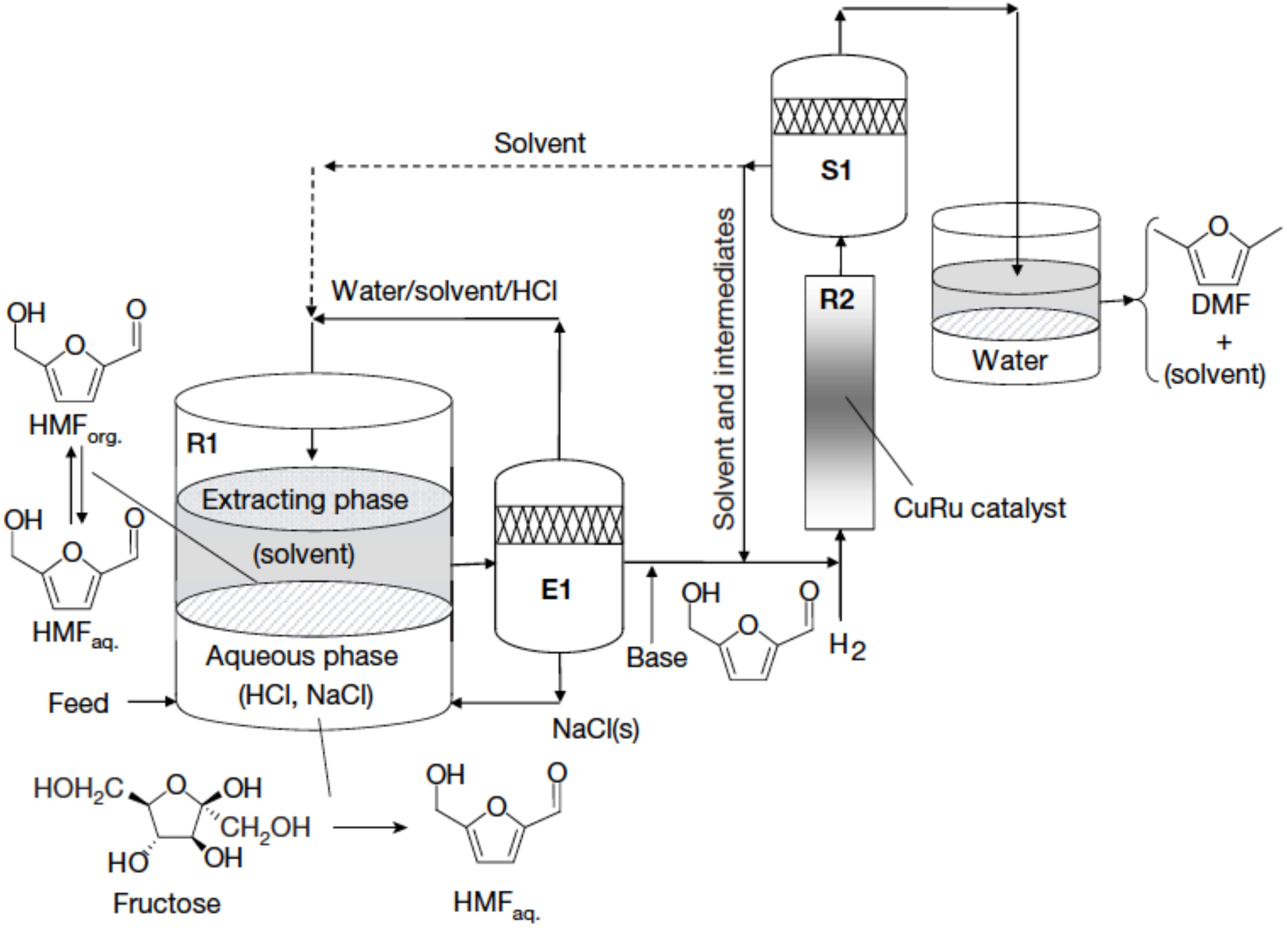
- Dimethylfuran (DMF) has high energy density, suitable as a liquid transportation fuel



Roman-Leshkov, Y.; Barrett, C. J.; Liu, Z. Y.; Dumesic, J. A. *Nature* **2007**, *447*, 982.

Dumesic's Integrated Method Converting Fructose to Dimethylfuran

- Schematic diagram of the process for conversion of fructose to DMF



Roman-Leshkov, Y.; Barrett, C. J.; Liu, Z. Y.; Dumesic, J. A. *Nature* **2007**, *447*, 982.

Dumesic's Integrated Method Converting Fructose to Dimethylfuran

- Results for HMF formation in the biphasic reactor

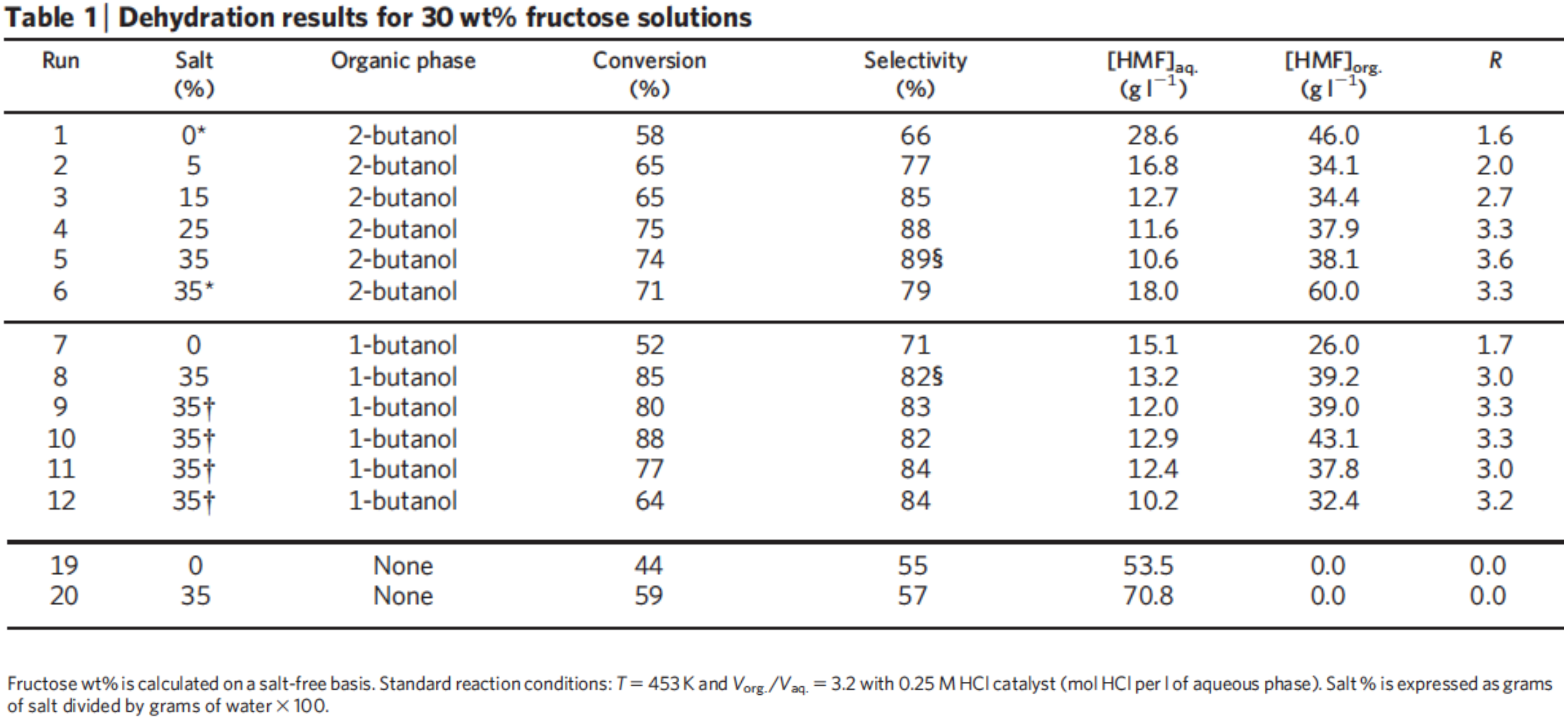


Table 1 | Dehydration results for 30 wt% fructose solutions

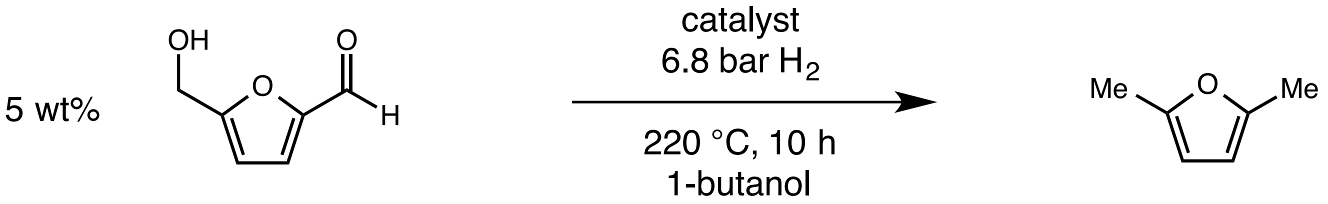
Run	Salt (%)	Organic phase	Conversion (%)	Selectivity (%)	$[\mathrm{HMF}]_{\mathrm{aq.}}$ ($\mathrm{g\,l^{-1}}$)	$[\mathrm{HMF}]_{\mathrm{org.}}$ ($\mathrm{g\,l^{-1}}$)	*R*
1	0*	2-butanol	58	66	28.6	46.0	1.6
2	5	2-butanol	65	77	16.8	34.1	2.0
3	15	2-butanol	65	85	12.7	34.4	2.7
4	25	2-butanol	75	88	11.6	37.9	3.3
5	35	2-butanol	74	89§	10.6	38.1	3.6
6	35*	2-butanol	71	79	18.0	60.0	3.3
7	0	1-butanol	52	71	15.1	26.0	1.7
8	35	1-butanol	85	82§	13.2	39.2	3.0
9	35†	1-butanol	80	83	12.0	39.0	3.3
10	35†	1-butanol	88	82	12.9	43.1	3.3
11	35†	1-butanol	77	84	12.4	37.8	3.0
12	35†	1-butanol	64	84	10.2	32.4	3.2
19	0	None	44	55	53.5	0.0	0.0
20	35	None	59	57	70.8	0.0	0.0

Fructose wt% is calculated on a salt-free basis. Standard reaction conditions: $T = 453$ K and $V_{\mathrm{org.}}/V_{\mathrm{aq.}} = 3.2$ with 0.25 M HCl catalyst (mol HCl per l of aqueous phase). Salt % is expressed as grams of salt divided by grams of water × 100.

Roman-Leshkov, Y.; Barrett, C. J.; Liu, Z. Y.; Dumesic, J. A. *Nature* **2007**, *447*, 982.

Dumesic's Integrated Method Converting Fructose to Dimethylfuran

Conversion of HMF to DMF under biphasic reactor conditions



Catalyst	**Precontacted with H_2O and NaCl**	**Conversion**	**Yield of DMF**	**Carbon Out/In**
$CuCrO_4$	No	100%	**61%**	92%
$CuCrO_4$	Yes (purified)	94%	**6%**	87%
$CuCrO_4$	Yes	18%	**0%**	82%

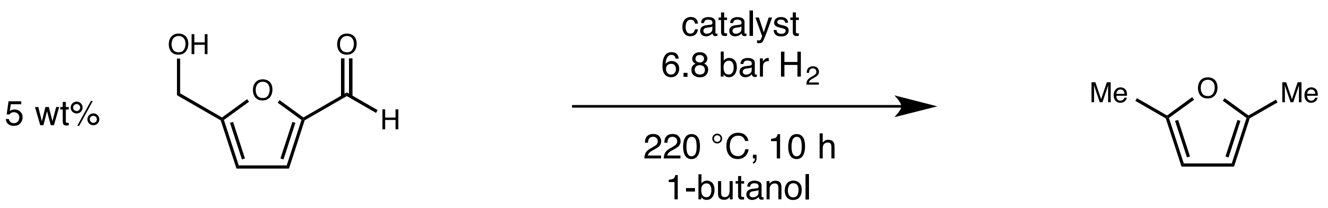
Chloride ions believed to deactivate $CuCrO_4$ catalyst

Postulated that a CuRu on carbon catalyst will retain hydrogenolysis behaviour
but be resistant to chloride deactivation

Roman-Leshkov, Y.; Barrett, C. J.; Liu, Z. Y.; Dumesic, J. A. *Nature* **2007**, *447*, 982.

Dumesic's Integrated Method Converting Fructose to Dimethylfuran

Conversion of HMF to DMF under biphasic reactor conditions



catalyst
6.8 bar H_2

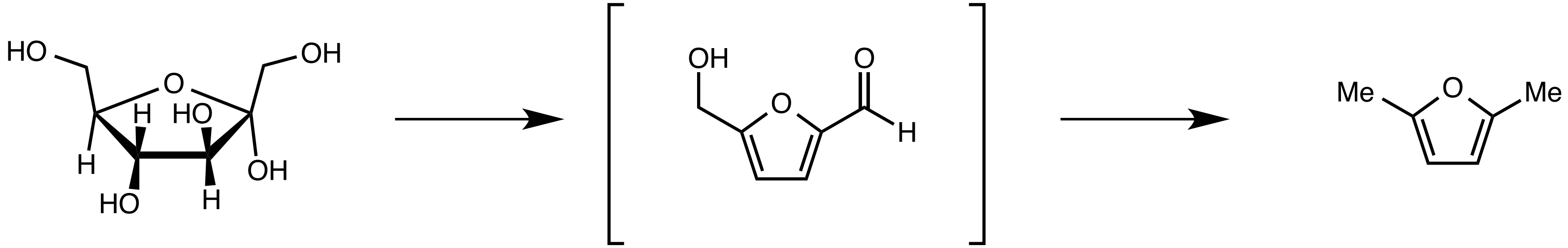
220 °C, 10 h
1-butanol

Catalyst	**Precontacted with H_2O and NaCl**	**Conversion**	**Yield of DMF**	**Carbon Out/In**
$CuCrO_4$	No	100%	**61%**	92%
$CuCrO_4$	Yes (purified)	94%	**6%**	87%
$CuCrO_4$	Yes	18%	**0%**	82%
3:1 CuRu/C	No	100%	**71%**	89%
3:1 CuRu/C	Yes (purified)	100%	**61%**	86%
3:1 CuRu/C	Yes	100%	**41%**	80%

Roman-Leshkov, Y.; Barrett, C. J.; Liu, Z. Y.; Dumesic, J. A. *Nature* **2007**, *447*, 982.

Dumesic's Integrated Method Converting Fructose to Dimethylfuran

- Synthesis of DMF from fructose important contribution to biofuel production



2,5-dimethylfuran has higher energy density than ethanol

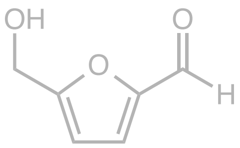
Energy required for separating DMF and 1-butanol is ~ 1/3 energy required to separate ethanol from aqueous solution following fermentation

Challenges remain in converting glucose directly (more available feedstock)

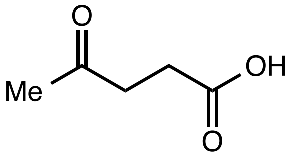
Toxicity of dimethylfuran has not been thoroughly studied

Roman-Leshkov, Y.; Barrett, C. J.; Liu, Z. Y.; Dumesic, J. A. *Nature* **2007**, *447*, 982.

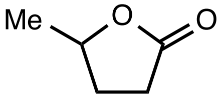
Platform Chemicals and Upgrading Strategies



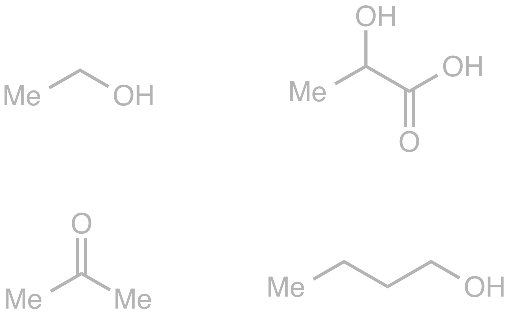
5-hydroxymethylfurfural (HMF)



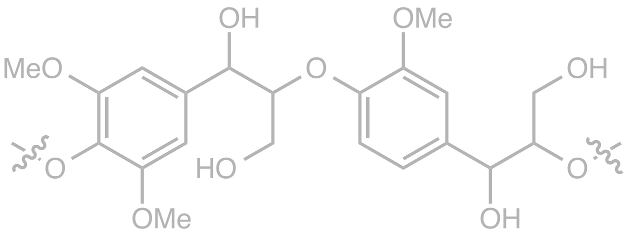
levulinic acid (LA)



γ-valerolactone (GVL)



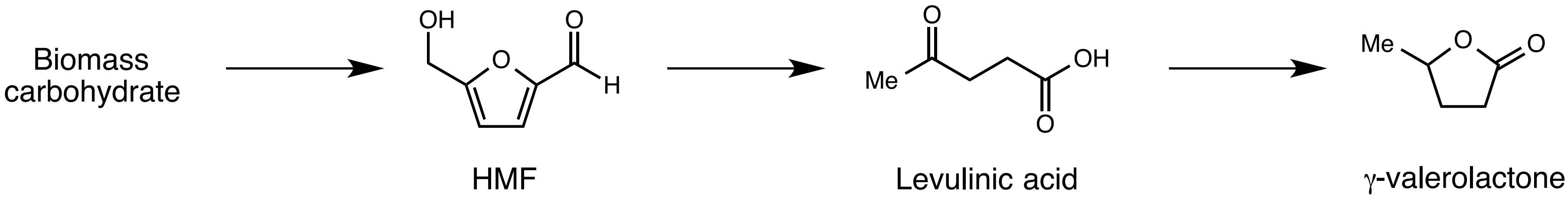
fermentation products



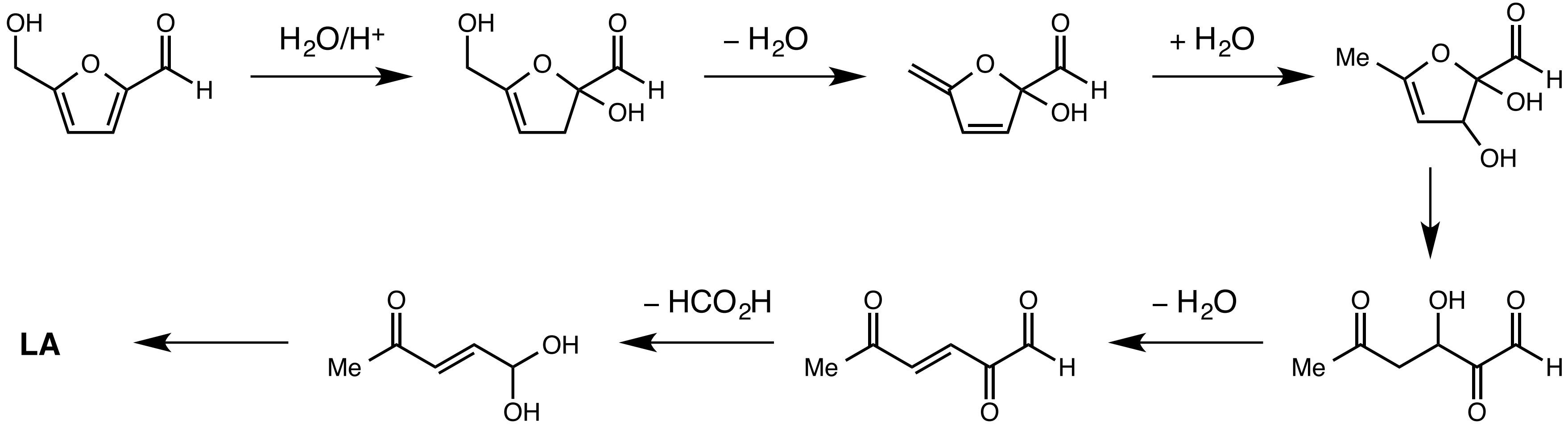
lignin

Horvath's First Generation Synthesis of γ-valerolactone

■ GVL can be obtained via levulinic acid, from HMF, from glucose



■ Proposed mechanism for conversion of HMF into LA under acidic conditions

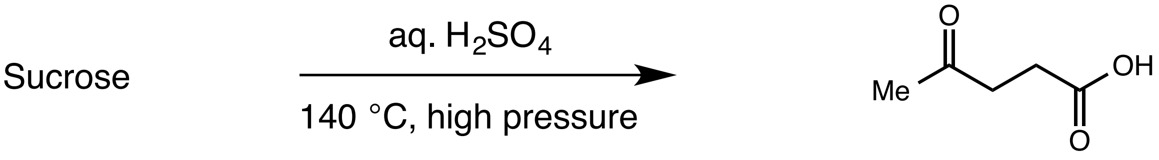


Horvath, I. T.; Mehdi, H.; Fabos, V.; Boda, L.; Mika, L. T. *Green Chem.* **2008**, *10*, 238.

Mehdi, H.; Fabos, V.; Tuba, R.; Bodor, A.; Mika, L. T.; Horvath, I. T. *Top. Catal.* **2008**, *48*, 49.

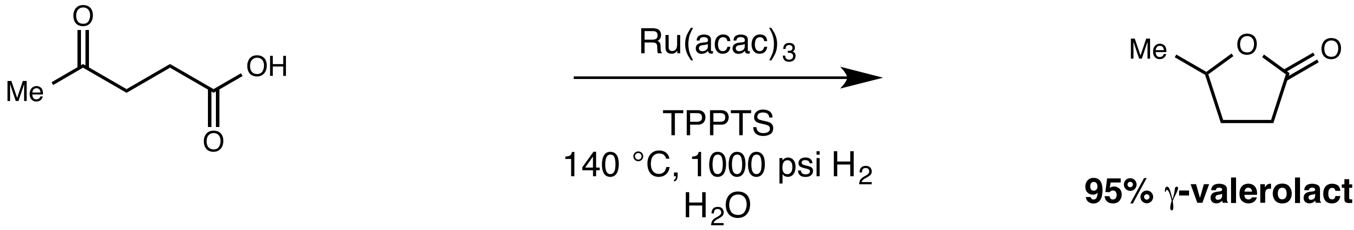
Horvath's First Generation Synthesis of γ-valerolactone

■ Direct synthesis of LA from sucrose

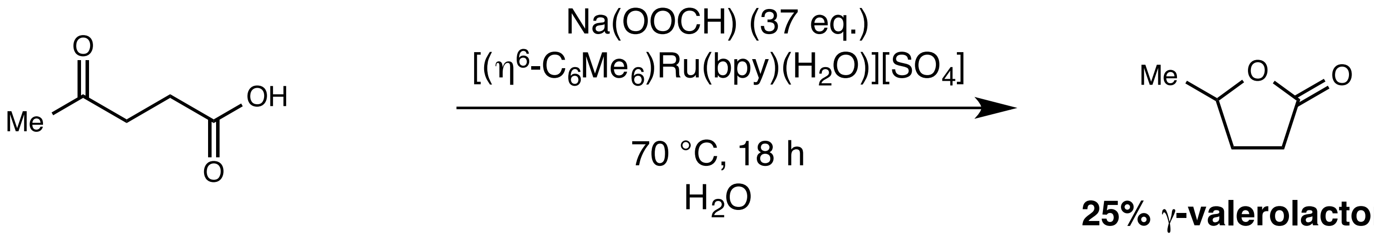


"40–50%" Levulinic acid

■ Conversion of LA to GVL



95% γ-valerolactone



25% γ-valerolactone

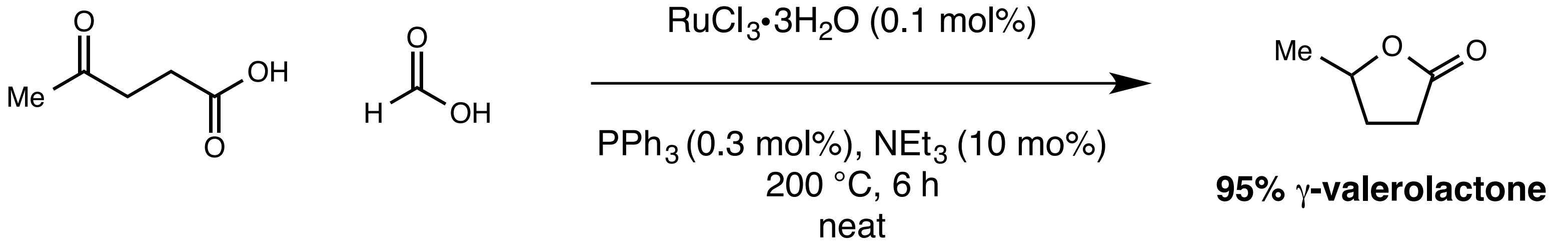
25% 1,4-pentanediol

Horvath, I. T.; Mehdi, H.; Fabos, V.; Boda, L.; Mika, L. T. *Green Chem.* **2008**, *10*, 238.

Mehdi, H.; Fabos, V.; Tuba, R.; Bodor, A.; Mika, L. T.; Horvath, I. T. *Top. Catal.* **2008**, *48*, 49.

Guo and Fu's Improved Transfer Hydrogenation to γ-valerolactone

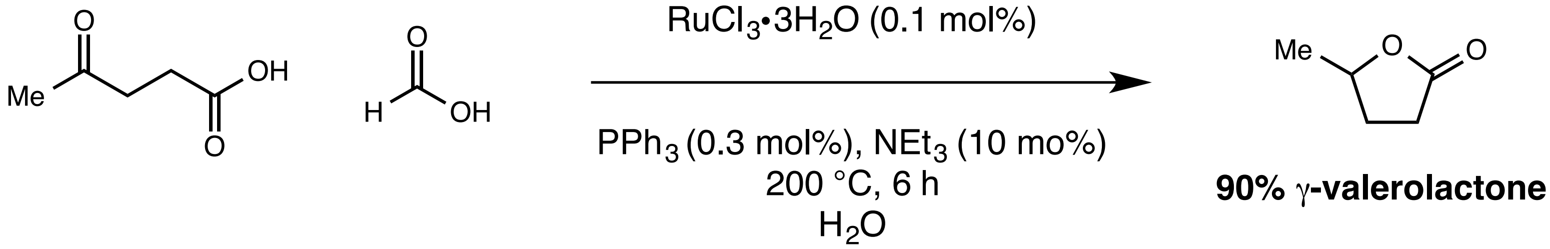
■ Synthesis of GVL using formic acid as H_2 source


$RuCl_3$•$3H_2O$ (0.1 mol%)

PPh_3 (0.3 mol%), NEt_3 (10 mo%)
200 °C, 6 h
neat

95% γ-valerolactone

Aqueous conditions


$RuCl_3$•$3H_2O$ (0.1 mol%)

PPh_3 (0.3 mol%), NEt_3 (10 mo%)
200 °C, 6 h
H_2O

90% γ-valerolactone

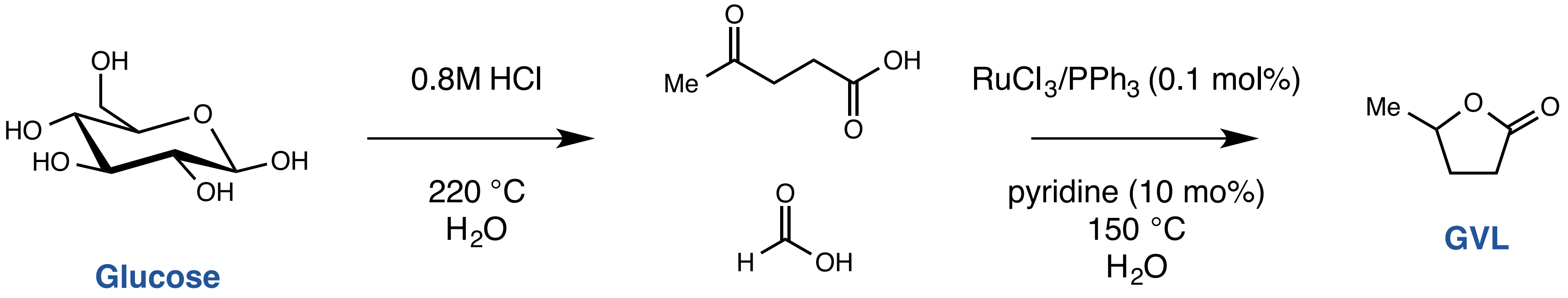
Observed increase in pressure: 0.1 MPa to 8 MPa over 20 minutes

Decomposition of formic acid to H_2 and CO_2

Deng, L.; Li, J.; Lai, D.-M.; Fu, Y.; Guo, Q.-X. *Angew. Chem. Int. Ed.* **2009**, *48*, 6529.

Guo and Fu's Improved Transfer Hydrogenation to γ-valerolactone

■ Direct synthesis of GVL from glucose



48% yield
over 2 steps

Guo and Fu demonstrate direct two step conversion of glucose feedstock to γ-valerolactone

LA and formic acid undergo pH neutralization and distillation (to remove some H_2O) between transformations

Deng, L.; Li, J.; Lai, D.-M.; Fu, Y.; Guo, Q.-X. *Angew. Chem. Int. Ed.* **2009**, *48*, 6529.

Guo and Fu's Improved Transfer Hydrogenation to γ-valerolactone

- CO_2 is an essential additive in the hydrogenation of LA to GVL

Performing the reaction with external H_2 drops efficiency to 45% from 90% with formic acid

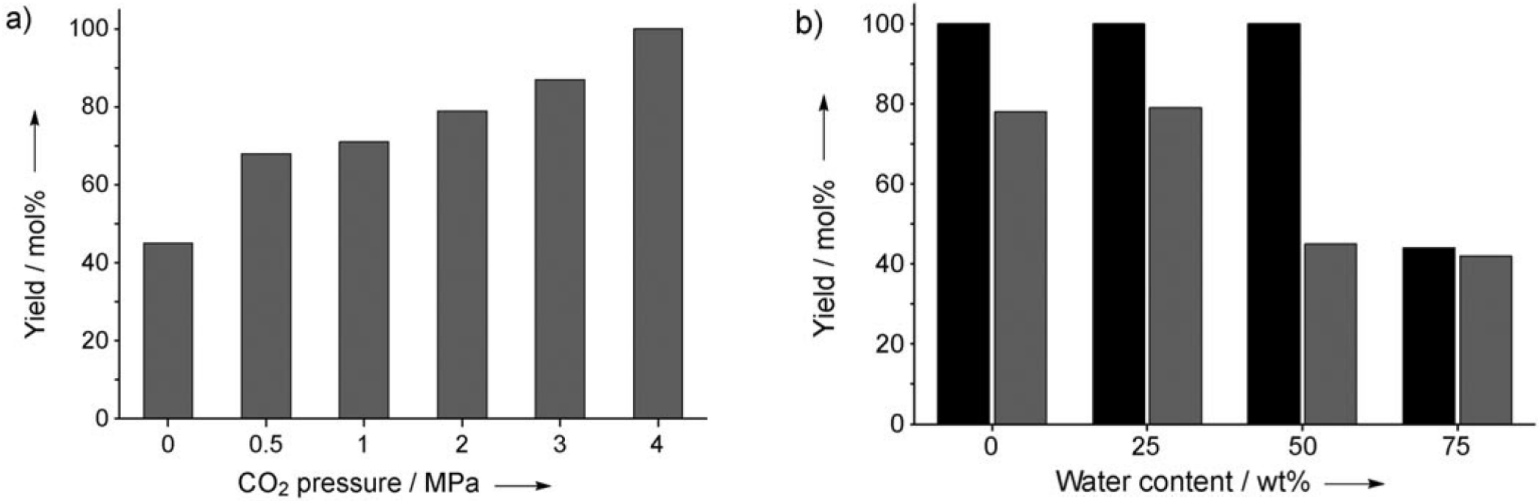


Figure 1. Effect of CO_2 on the hydrogenation of LA. Reaction conditions: 150 °C, 12 h, 200 mmol LA, 20 mmol pyridine, 0.2 mmol $RuCl_3$, 0.6 mmol PPh_3, and 4 MPa H_2. a) Reaction conducted in 50 wt% water; b) Reaction conducted with 4 MPa CO_2 (black) and without CO_2 (gray).

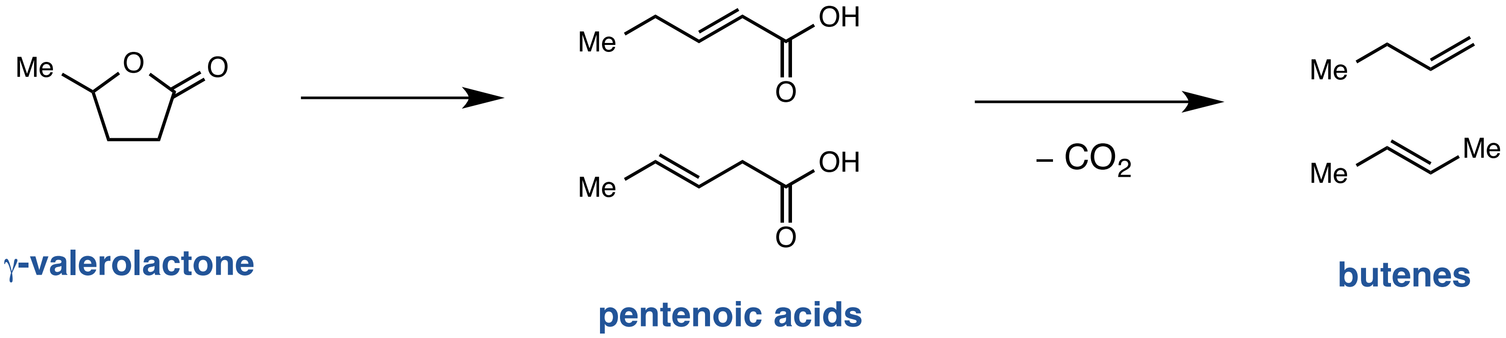
Role of CO_2 in Ru-catalyzed hydrogenation is unexplained

Deng, L.; Li, J.; Lai, D.-M.; Fu, Y.; Guo, Q.-X. *Angew. Chem. Int. Ed.* **2009**, *48*, 6529.

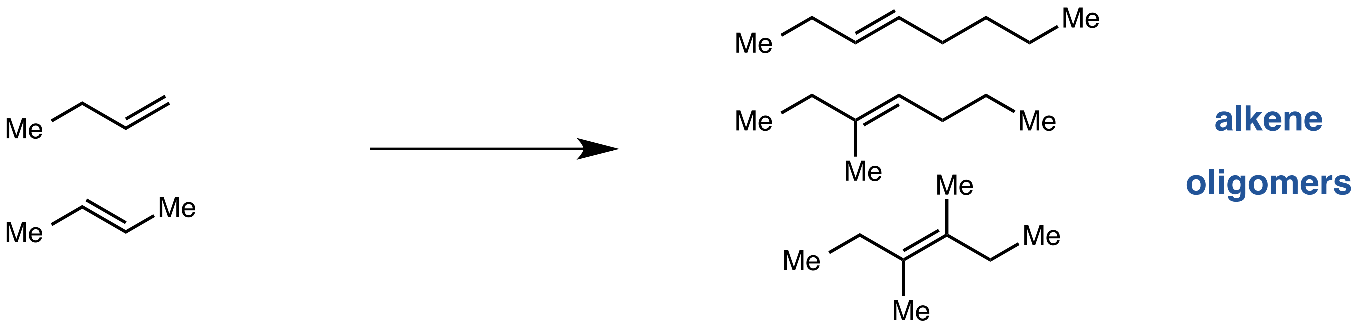
Dumesic's Integrated System Converting GVL to Alkenes

■ Decarboxylation followed by oligomerization

Reactor 1



Reactor 2



Dumesic proposes an integrated system to produce high value C_{8+} alkenes while controlling CO_2 streams

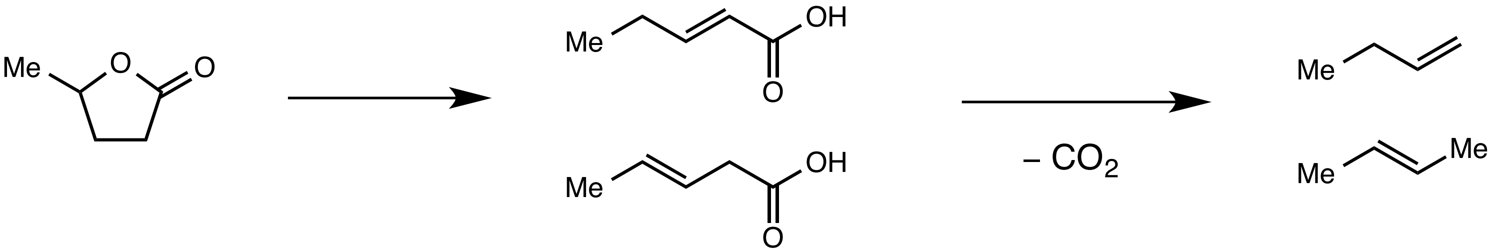
No external H_2 needed

Bond, J. Q.; Alonso, D. M.; Wang, D.; West, R. M.; Dumesic, J. A. *Science* **2010**, *327*, 1110.

Dumesic's Integrated System Converting GVL to Alkenes

■ Decarboxylation followed by oligomerization

Reactor 1



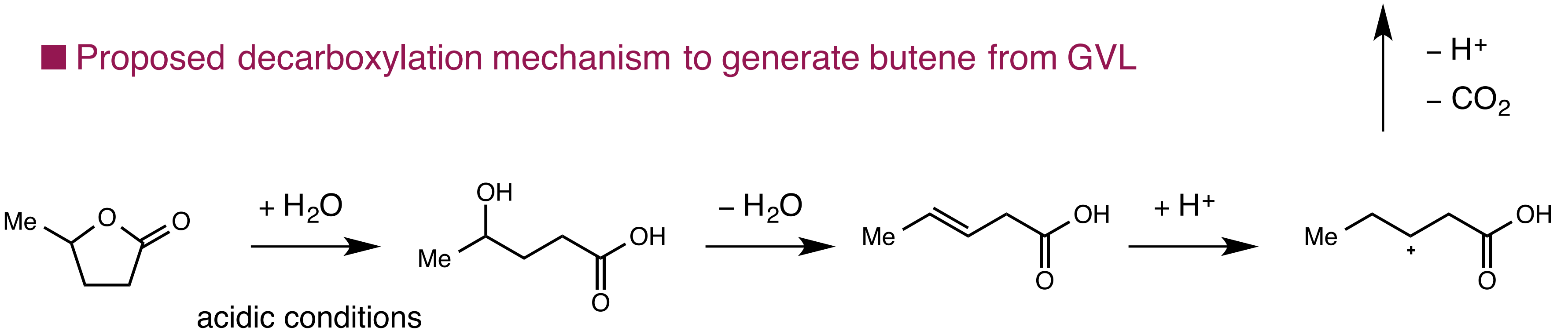
$- CO_2$

γ-valerolactone

pentenoic acids

butenes

■ Proposed decarboxylation mechanism to generate butene from GVL



$+ H_2O$

acidic conditions

$- H_2O$

$+ H^+$

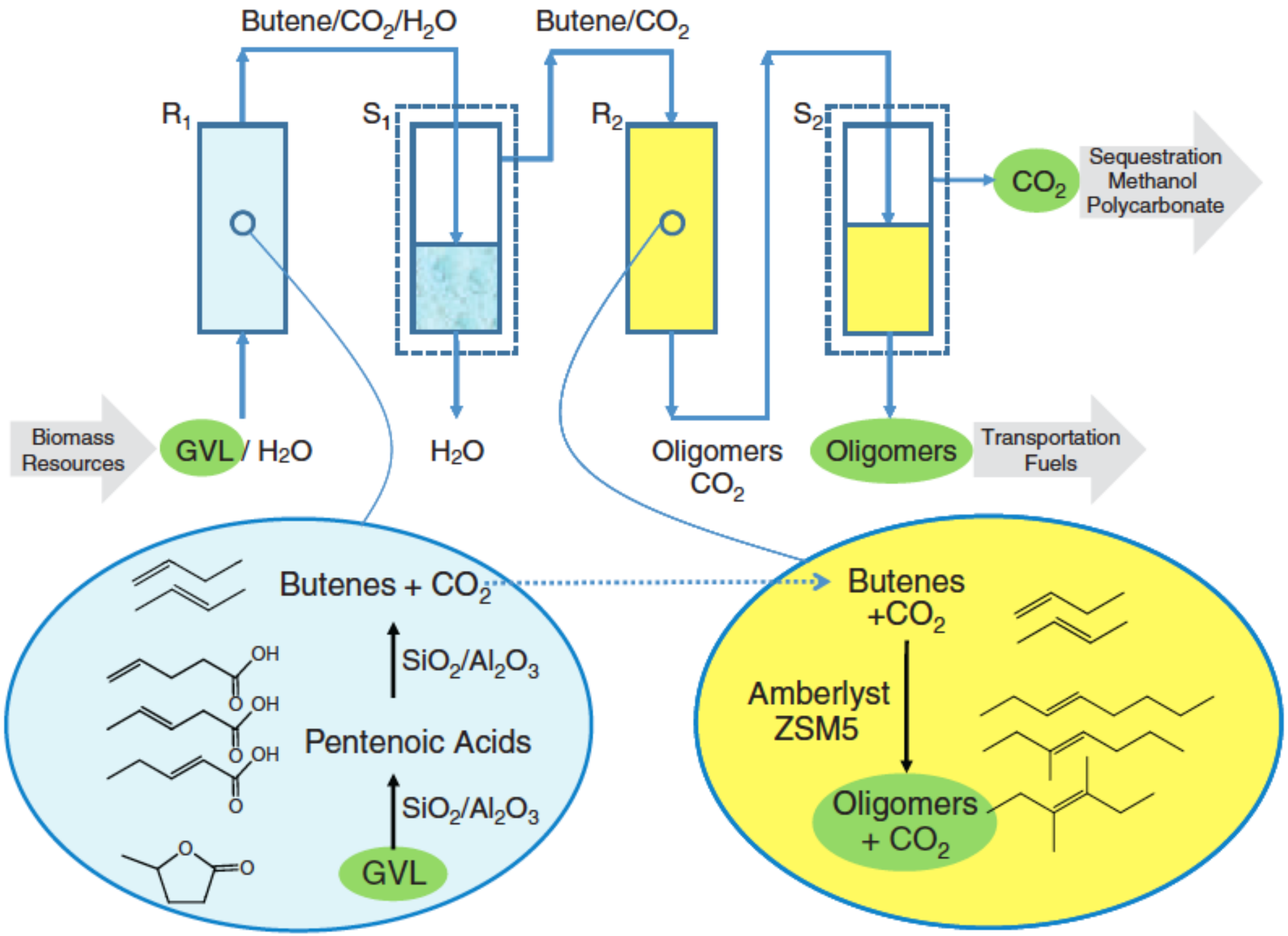
$- H^+$

$- CO_2$

Bond, J. Q.; Alonso, D. M.; Wang, D.; West, R. M.; Dumesic, J. A. *Science* **2010**, *327*, 1110.

Dumesic's Integrated System Converting GVL to Alkenes

- Integrated system - two flow reactors, two phase separators



Bond, J. Q.; Alonso, D. M.; Wang, D.; West, R. M.; Dumesic, J. A. *Science* **2010**, *327*, 1110.

Dumesic's Integrated System Converting GVL to Alkenes

- Dumesic and coworkers optimized each process individually first
- Efficient levels of C_{8+} alkenes are observed after optimizing conditions for integrated system

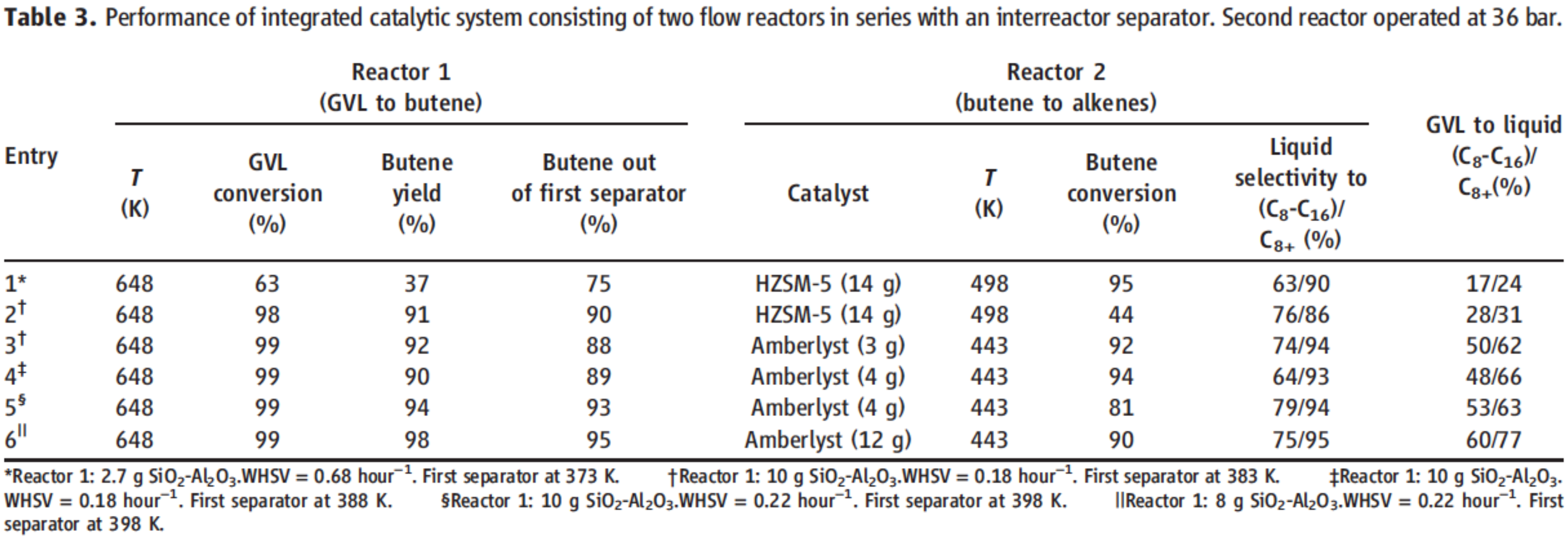


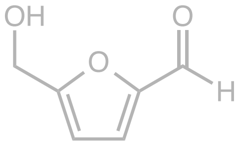
Table 3. Performance of integrated catalytic system consisting of two flow reactors in series with an interreactor separator. Second reactor operated at 36 bar.

Entry	Reactor 1 (GVL to butene)				Reactor 2 (butene to alkenes)				GVL to liquid $(C_8\text{-}C_{16})/C_{8+}$(%)
	T (K)	GVL conversion (%)	Butene yield (%)	Butene out of first separator (%)	Catalyst	*T* (K)	Butene conversion (%)	Liquid selectivity to $(C_8\text{-}C_{16})/C_{8+}$ (%)	
1*	648	63	37	75	HZSM-5 (14 g)	498	95	63/90	17/24
2†	648	98	91	90	HZSM-5 (14 g)	498	44	76/86	28/31
3†	648	99	92	88	Amberlyst (3 g)	443	92	74/94	50/62
4‡	648	99	90	89	Amberlyst (4 g)	443	94	64/93	48/66
5§	648	99	94	93	Amberlyst (4 g)	443	81	79/94	53/63
6‖	648	99	98	95	Amberlyst (12 g)	443	90	75/95	60/77

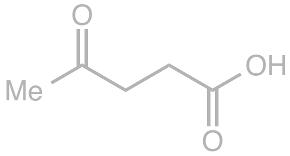
*Reactor 1: 2.7 g SiO_2-Al_2O_3.WHSV = 0.68 $hour^{-1}$. First separator at 373 K. †Reactor 1: 10 g SiO_2-Al_2O_3.WHSV = 0.18 $hour^{-1}$. First separator at 383 K. ‡Reactor 1: 10 g SiO_2-Al_2O_3. WHSV = 0.18 $hour^{-1}$. First separator at 388 K. §Reactor 1: 10 g SiO_2-Al_2O_3.WHSV = 0.22 $hour^{-1}$. First separator at 398 K. ‖Reactor 1: 8 g SiO_2-Al_2O_3.WHSV = 0.22 $hour^{-1}$. First separator at 398 K.

Bond, J. Q.; Alonso, D. M.; Wang, D.; West, R. M.; Dumesic, J. A. *Science* **2010**, *327*, 1110.

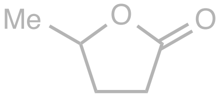
Platform Chemicals and Upgrading Strategies



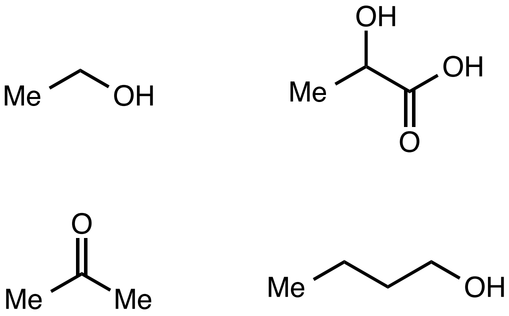
5-hydroxymethylfurfural (HMF)



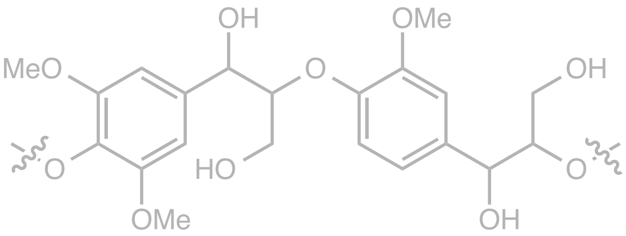
levulinic acid (LA)



γ-valerolactone (GVL)



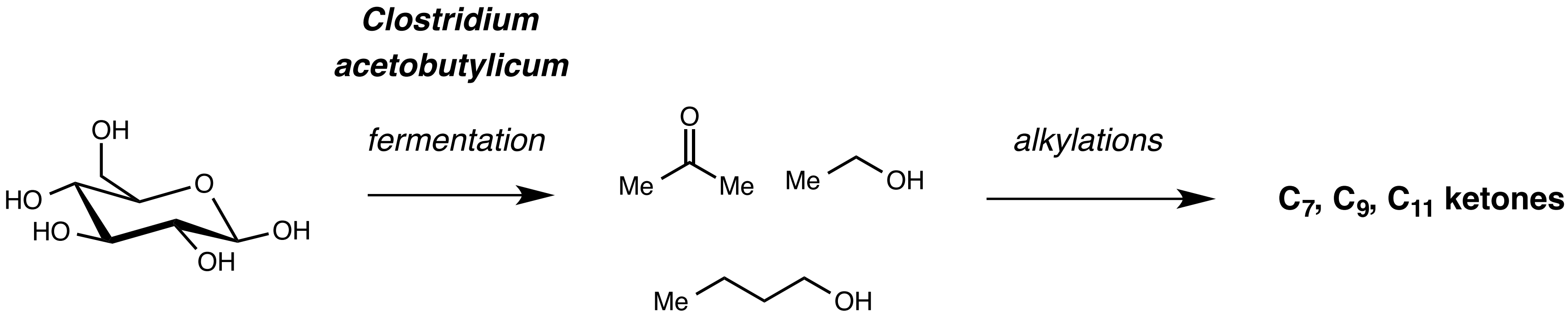
fermentation products



lignin

Toste's System Upgrades ABE Products to Ketones

- Toste and coworkers proposed upgrading products of ABE fermentation



glucose

acetone, ethanol, butanol

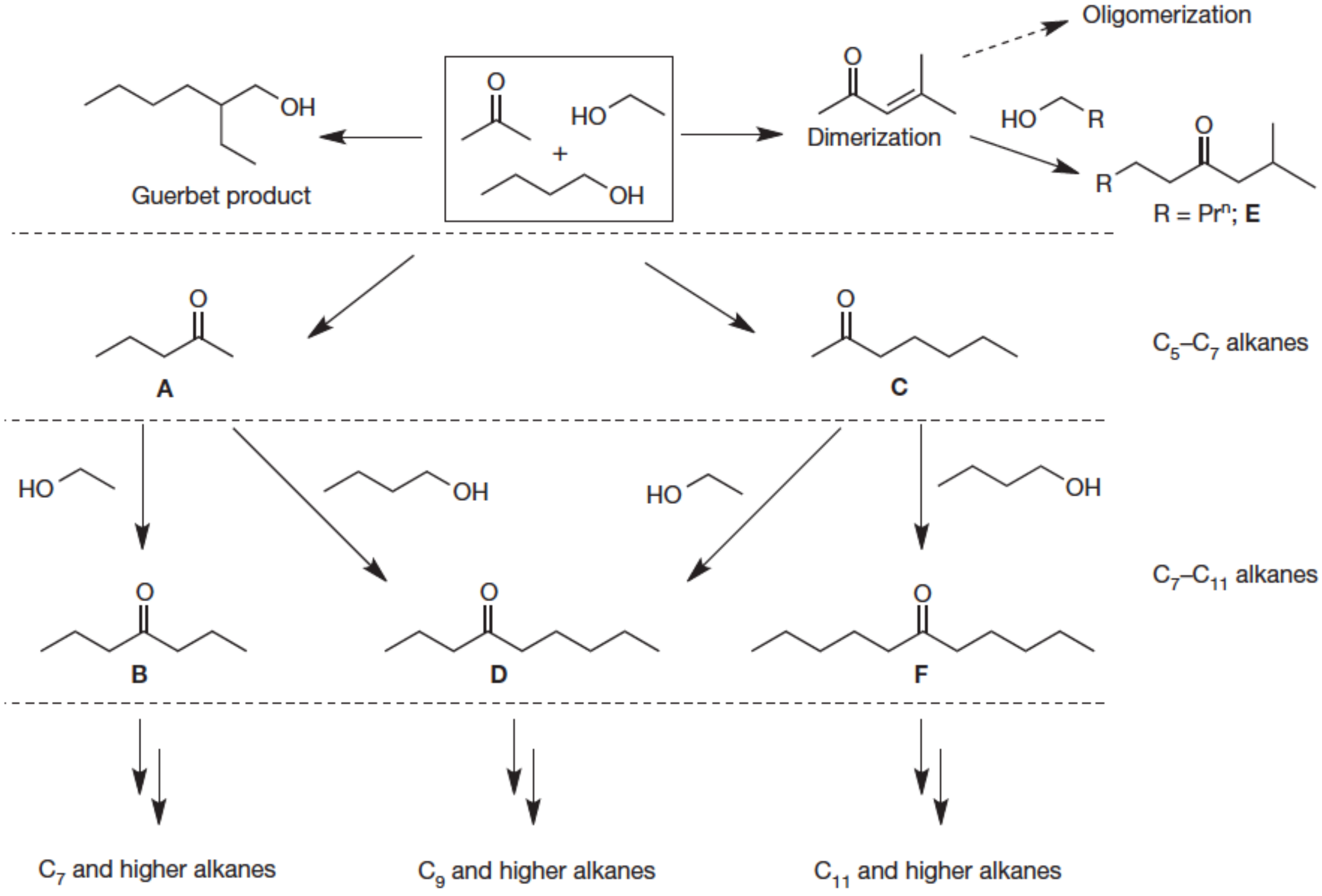
Transfer hydrogenation strategy enables C-C bond formation via consecutive aldol condensations

Upgrading strategy increases energy density of ABE fermentation products

Anbarasan, P.; Baer, Z. C.; Sreekumar, S.; Gross, E.; Binder, J. B.; Blanch, H. W.; Clark, D. S.; Toste, F. D. *Nature* **2012**, *491*, 235.

Toste's System Upgrades ABE Products to Ketones

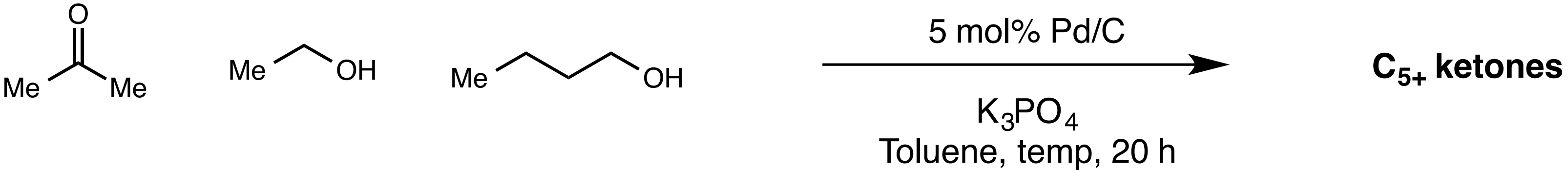
- General approach to ABE upgrading strategy



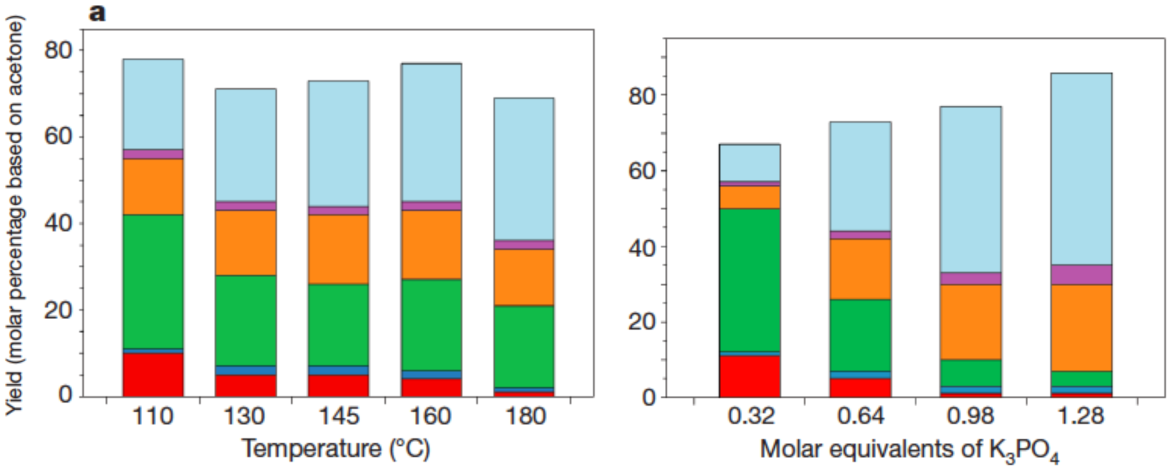
Anbarasan, P.; Baer, Z. C.; Sreekumar, S.; Gross, E.; Binder, J. B.; Blanch, H. W.; Clark, D. S.; Toste, F. D. *Nature* **2012**, *491*, 235.

Toste's System Upgrades ABE Products to Ketones

- Pd/C optimal catalyst, K_3PO_4 optimal base for transformation



acetone:ethanol:butanol (2.3:1:3.7)

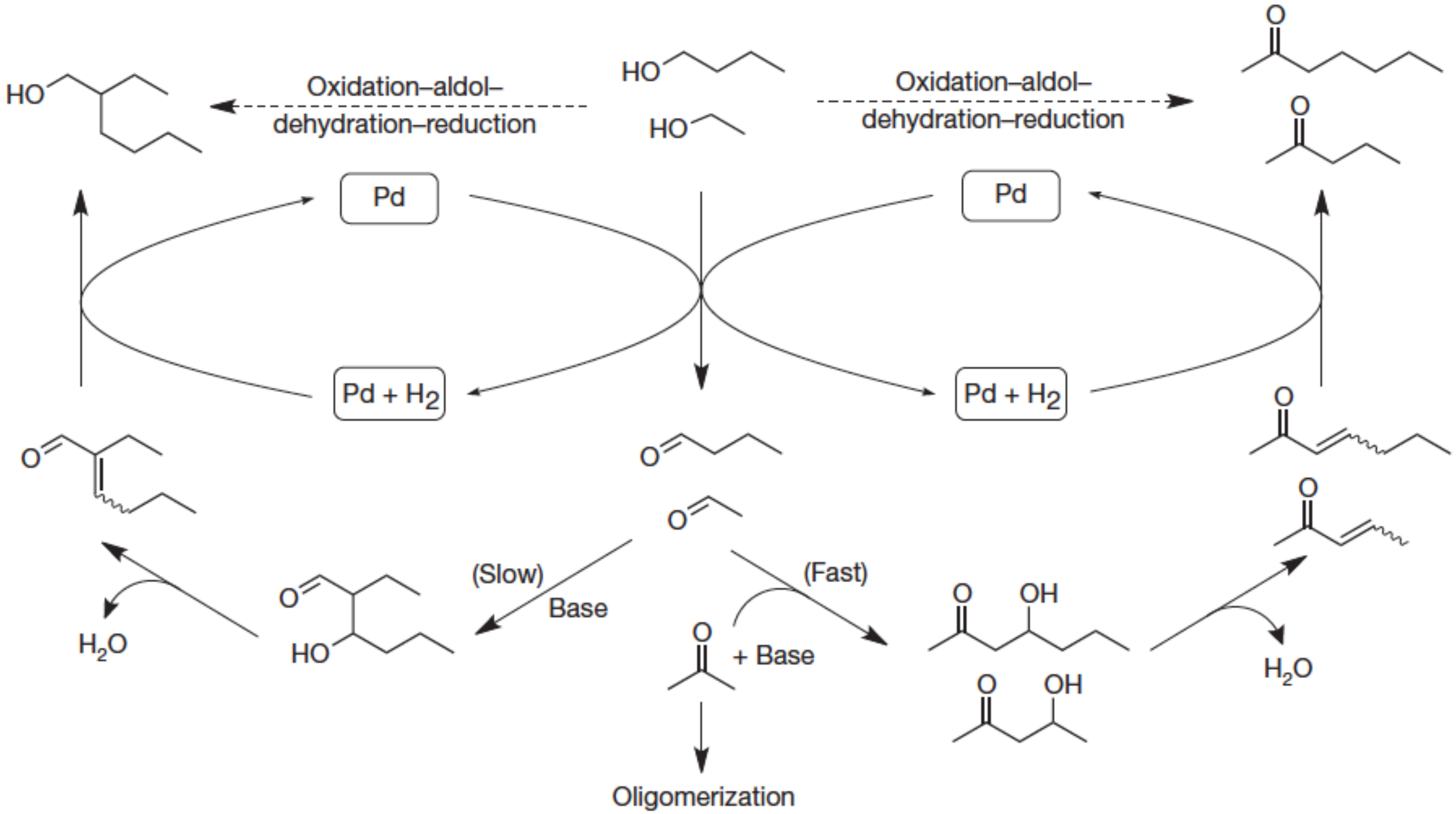


Red = pentan-2-one
Dark blue = heptan-4-one
Green = heptan-2-one
Orange = nonan-4-one
Purple = 2-methylnonan-4-one
Light Blue = undecan-6-one

Anbarasan, P.; Baer, Z. C.; Sreekumar, S.; Gross, E.; Binder, J. B.; Blanch, H. W.; Clark, D. S.; Toste, F. D. *Nature* **2012**, *491*, 235.

Toste's System Upgrades ABE Products to Ketones

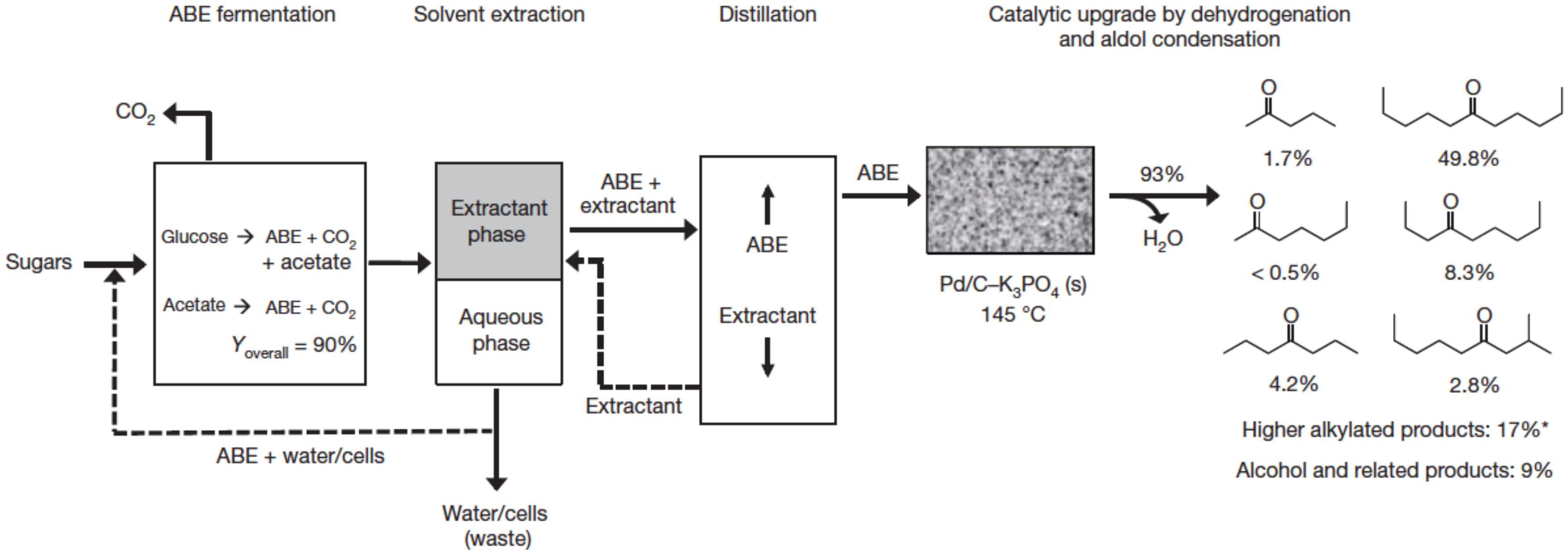
■ Proposed mechanism via palladium transfer hydrogenation catalysis



Anbarasan, P.; Baer, Z. C.; Sreekumar, S.; Gross, E.; Binder, J. B.; Blanch, H. W.; Clark, D. S.; Toste, F. D. *Nature* **2012**, *491*, 235.

Toste's System Upgrades ABE Products to Ketones

Diagram of Toste's proposed reactor for integrated fermentation–alkylation system



Glyceryl tributyrate additive enables more facile extraction of acetone and butanol from aqueous phase

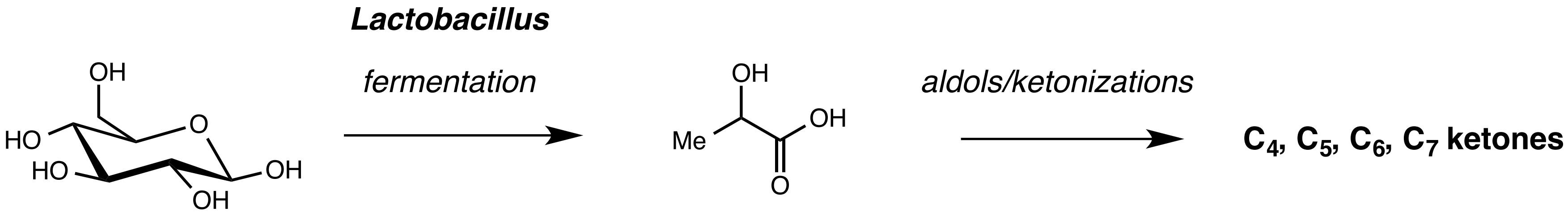
Assuming complete recovery of ABE in extraction step, 105g glucose would result in ~20 g C_7–C_{15} products

Represents ~38% conversion of carbon from glucose feed into high-value fuel ketones

Anbarasan, P.; Baer, Z. C.; Sreekumar, S.; Gross, E.; Binder, J. B.; Blanch, H. W.; Clark, D. S.; Toste, F. D. *Nature* **2012**, *491*, 235.

Lactic Acid Can be Upgraded to Ketones

- Dumesic demonstrates route to high-value ketones from lactic acid feedstock


Lactobacillus

fermentation

aldols/ketonizations

C_4, C_5, C_6, C_7 ketones

glucose

lactic acid

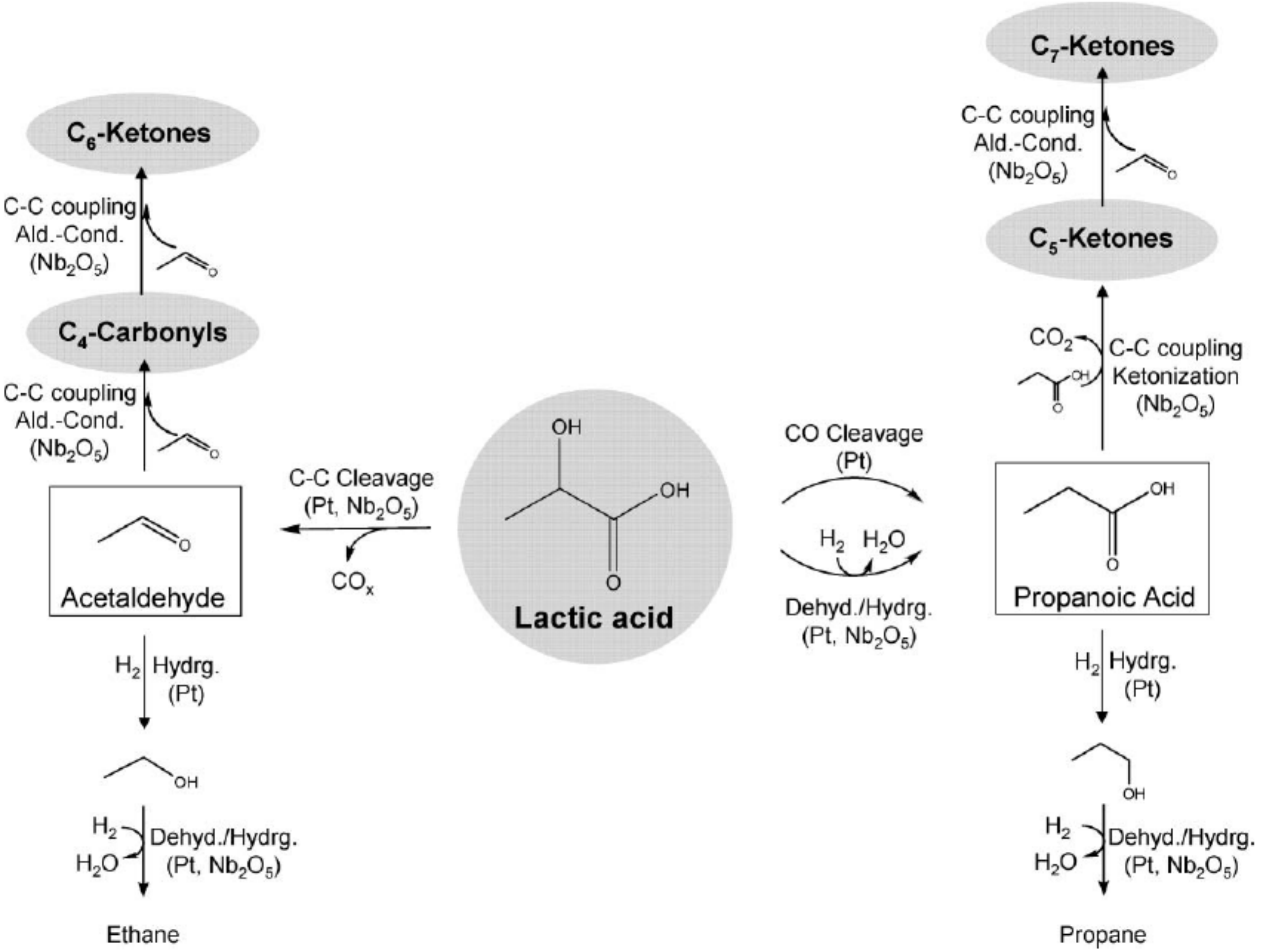
Lactic acid upgrading strategy involves partial reduction of oxygen content, followed by upgrading

Divergent mechanistic strategies via propanoic acid and acetaldehyde intermediates

Serrano-Ruiz, J. C.; Dumesic, J. A. *Green Chem.* **2009**, *11*, 1101.

Lactic Acid Can be Upgraded to Ketones

- Acetaldehyde and propanoic acid intermediates en route to ketones

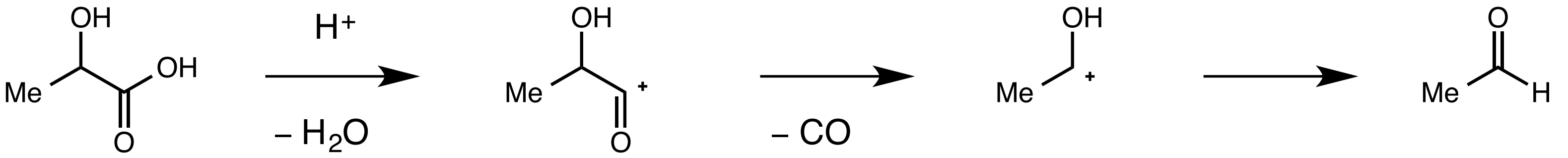


Serrano-Ruiz, J. C.; Dumesic, J. A. *Green Chem.* **2009**, *11*, 1101.

Lactic Acid Can be Upgraded to Ketones

- Interesting mechanistic pathways with Pt/Nb catalyst under high temperature and pressure

  - Proposed by Antal and Maitland Jones (with H_2SO_4, 385 °C, 5000 psi)

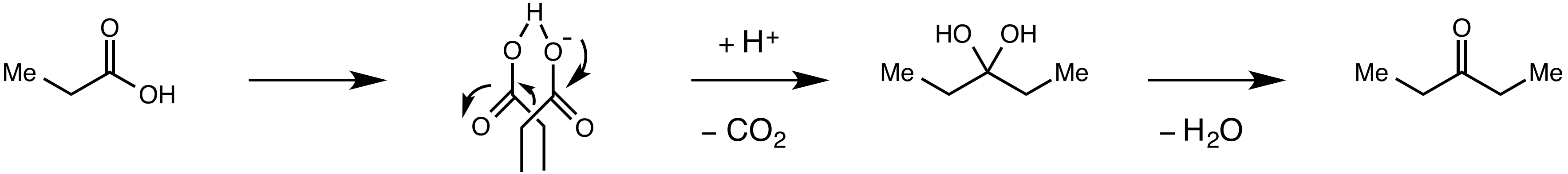


lactic acid

acetaldehyde

Mok, W. S.-L.; Antal, M. J.; Jones, M. *J. Org. Chem.* **1989**, *54*, 4596.

  - Ketonization of carboxylic acids - concerted decarboxylation–nucleophilic attack



2x propanoic acid

3-pentanone

Renz, M. *Eur. J. Org. Chem.* **2005**, 979.

Serrano-Ruiz, J. C.; Dumesic, J. A. *Green Chem.* **2009**, *11*, 1101.

Lactic Acid Can be Upgraded to Ketones

- Conversion of lactic acid to diverse mix of C_2–C_7 alcohols and ketones

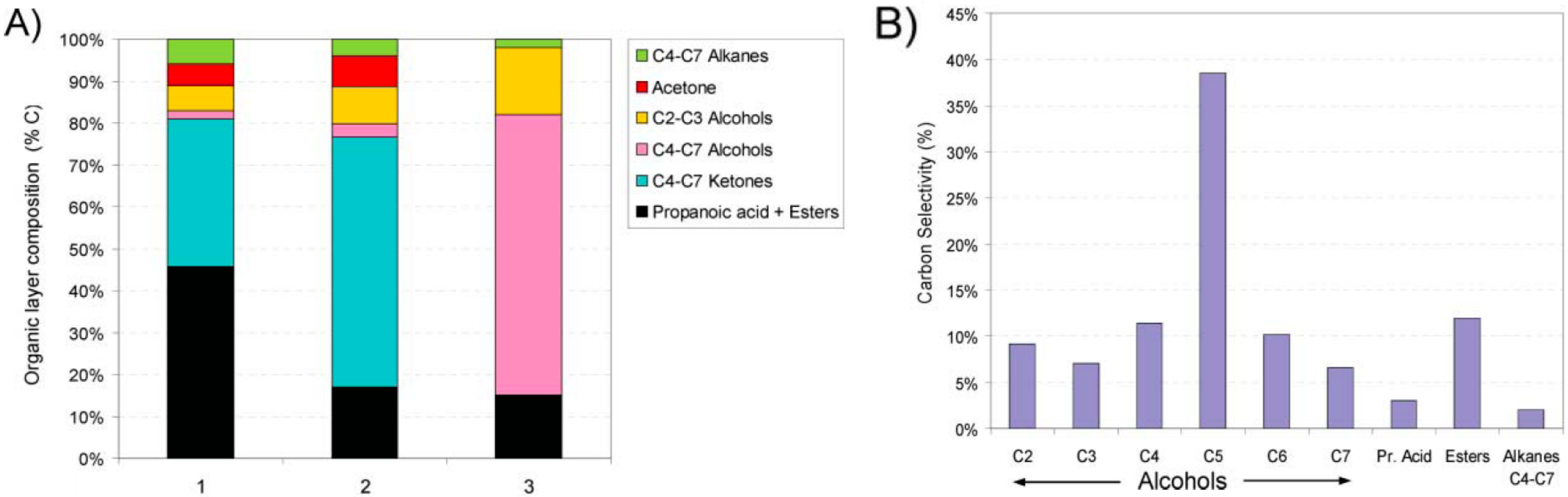
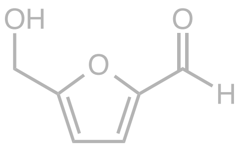


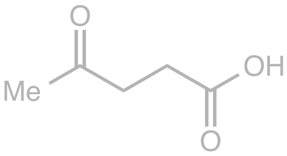
Fig. 2 A) Composition of the organic layer obtained for the conversion of a 60 wt% solution of lactic acid in water over 1: Pt(0.1%)/Nb_2O_5 at 623 K, 57 bar and WHSV = 1.7 h^{-1}; 2: Pt(0.1%)/Nb_2O_5 + $Ce_{0.5}Zr_{0.5}O_2$ double bed at 623 K, 57 bar and WHSV = 1.7 h^{-1} (based on first bed); 3: organic layer obtained from 2 after hydrogenation over Ru(5%)/C at 373 K, 35 bar and WHSV = 1.3 h^{-1} (H_2 co-feed at 50 cm^3(STP)/min). B) Composition of organic effluent obtained from 3; C_2–C_7 represent the number of carbons of the corresponding alcohols.

Serrano-Ruiz, J. C.; Dumesic, J. A. *Green Chem.* **2009**, *11*, 1101.

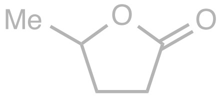
Platform Chemicals and Upgrading Strategies



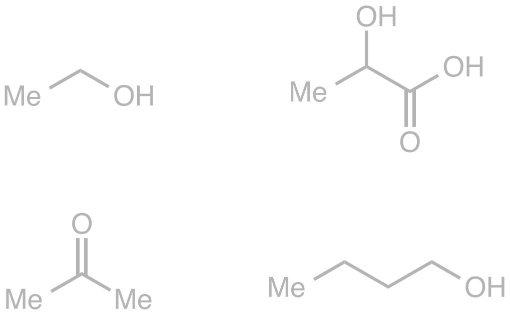
5-hydroxymethylfurfural (HMF)



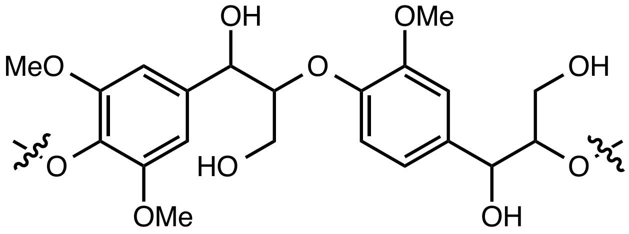
levulinic acid (LA)



γ-valerolactone (GVL)



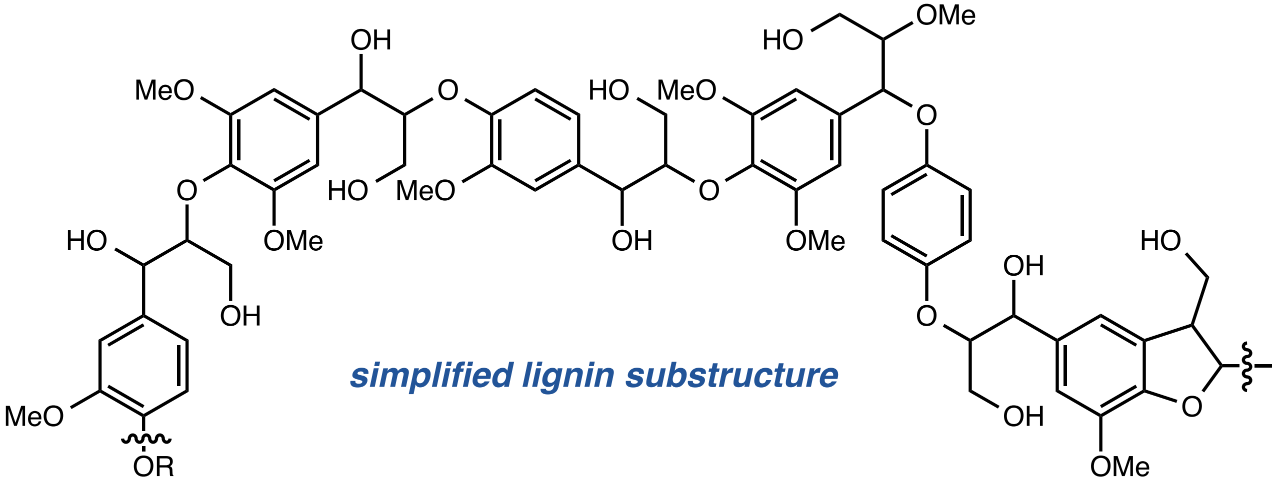
fermentation products



lignin

Lignin as a Biomass Feedstock

- Lignin is polymeric structure derived from coniferyl, coumaryl, and sinapyl alcohols



simplified lignin substructure

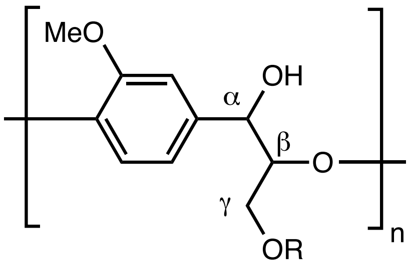
- Lignin is most often utilized by burning for heat/electricity production
- Methods to convert lignin into biofuels is mostly limited to pyrolysis methods (to make bio-oil)
- Degrading lignin in a controlled, selective fashion are in very early stages (model systems)

Xu, C.; Arancon, R. A. D.; Labidi, J.; Luque, R. *Chem. Soc. Rev.* **2014**, *43*, 7485.

Liu, C.; Wang, H.; Karim, A. M.; Sun, J.; Wang, Y. *Chem. Soc. Rev.* **2014**, *43*, 7594.

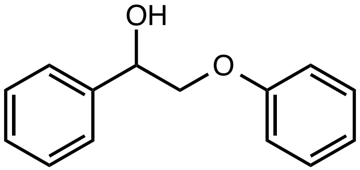
Ellman and Bergman Lignin C–O Bond Cleavage with Ruthenium

- Ellman and Bergman develop tandem dehydrogenation/reductive ether cleavage

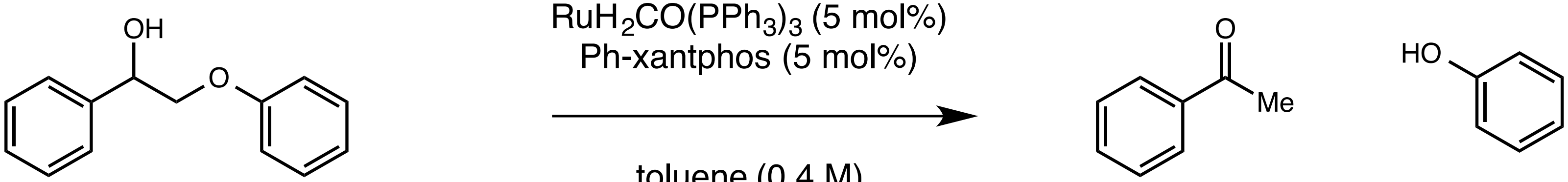


representative lignin polymer

≈



model system



$RuH_2CO(PPh_3)_3$ (5 mol%)
Ph-xantphos (5 mol%)

toluene (0.4 M)
135 °C, 1.75 h

β-O-4-ethanoaryl ether

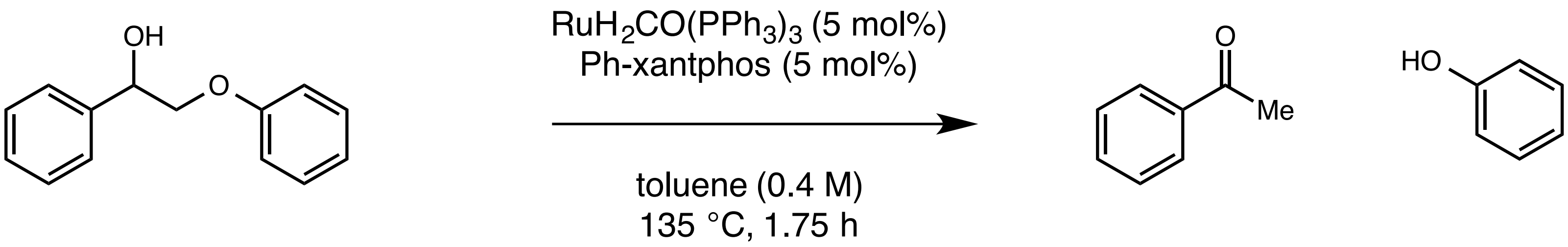
>99% yield

>99% yield

Nichols, J. M.; Bishop, L. M.; Bergman, R. G.; Ellman, J. A. *J. Am. Chem. Soc.* **2010**, *132*, 12554.

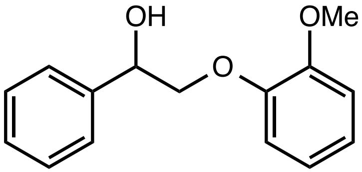
Ellman and Bergman Lignin C–O Bond Cleavage with Ruthenium

- Ellman and Bergman develop tandem dehydrogenation/reductive ether cleavage

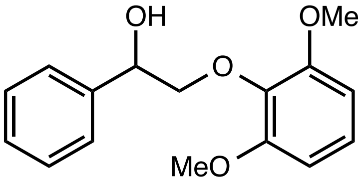


$RuH_2CO(PPh_3)_3$ (5 mol%)
Ph-xantphos (5 mol%)

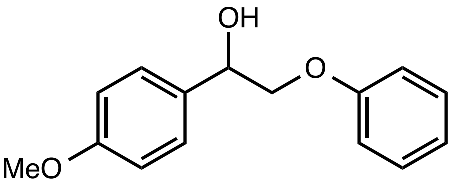
toluene (0.4 M)
135 °C, 1.75 h



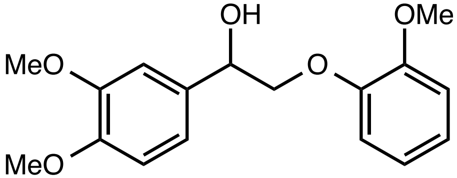
88%



62%



98%

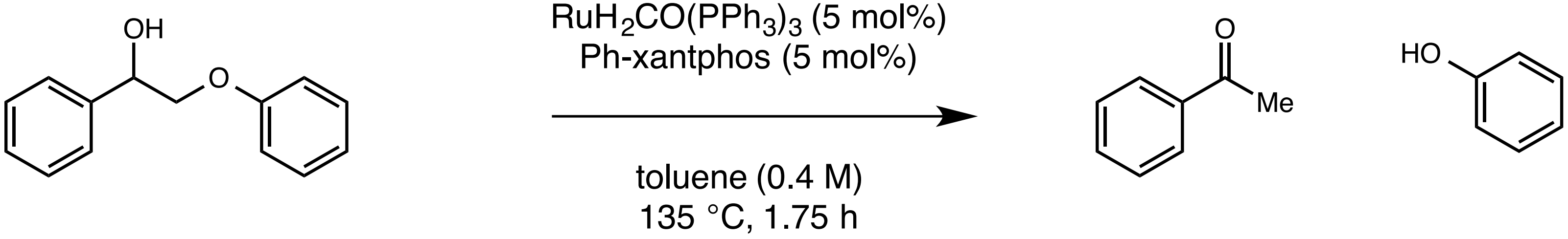


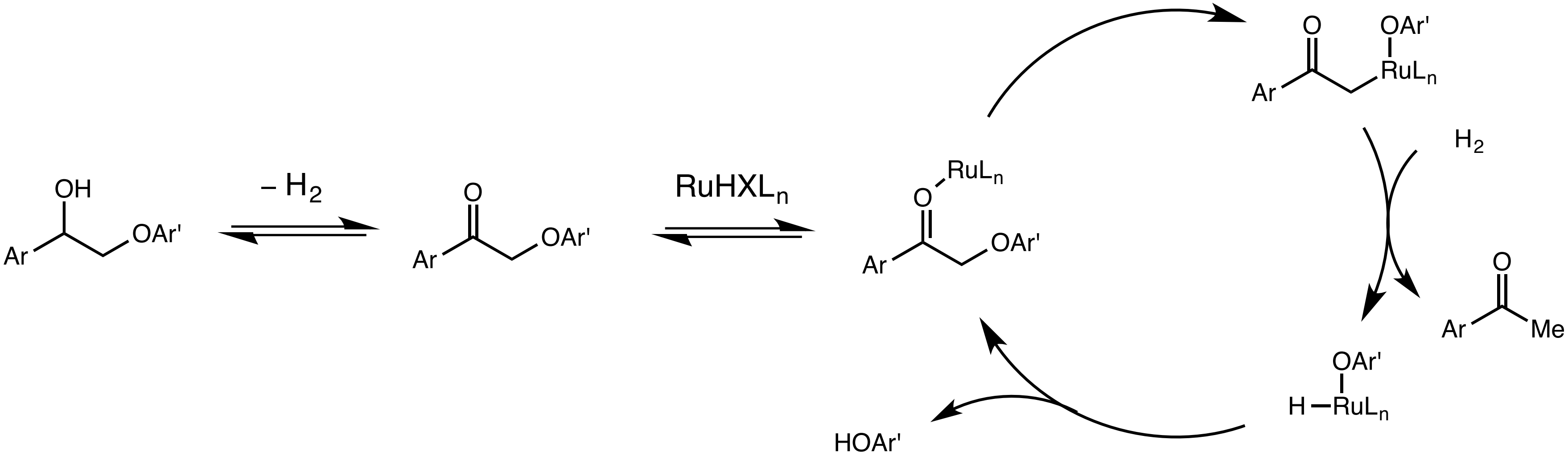
89%

Nichols, J. M.; Bishop, L. M.; Bergman, R. G.; Ellman, J. A. *J. Am. Chem. Soc.* **2010**, *132*, 12554.

Ellman and Bergman Lignin C–O Bond Cleavage with Ruthenium

■ Ellman and Bergman develop tandem dehydrogenation/reductive ether cleavage

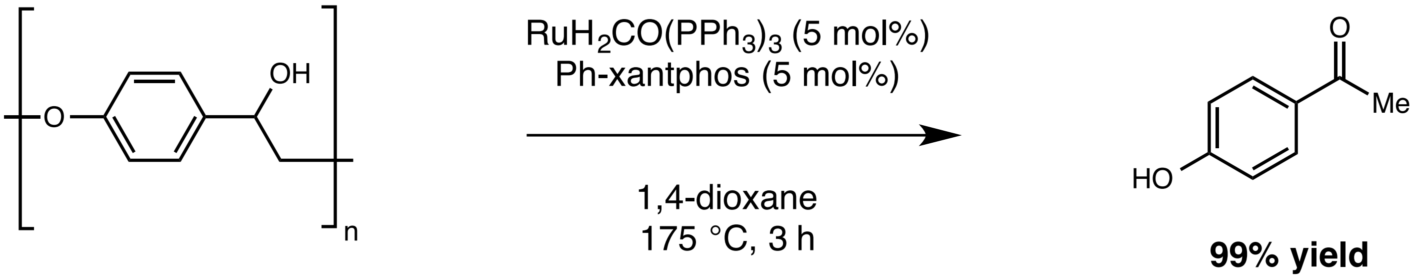




Nichols, J. M.; Bishop, L. M.; Bergman, R. G.; Ellman, J. A. *J. Am. Chem. Soc.* **2010**, *132*, 12554.

Ellman and Bergman Lignin C–O Bond Cleavage with Ruthenium

Depolymerization of lignin-related polymer

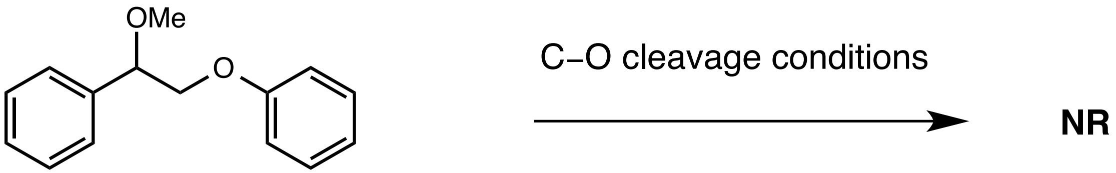


$RuH_2CO(PPh_3)_3$ (5 mol%)
Ph-xantphos (5 mol%)

1,4-dioxane
175 °C, 3 h

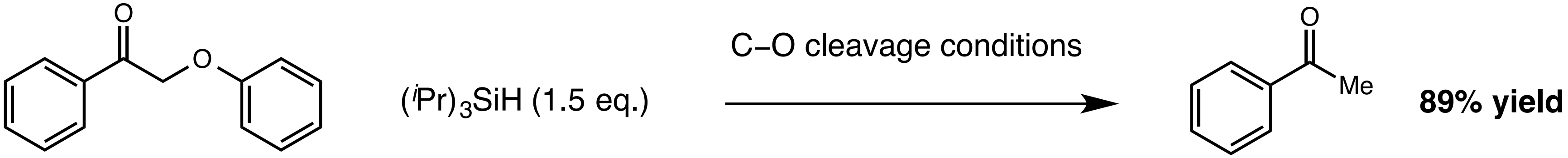
99% yield

Mechanistic considerations



C–O cleavage conditions

NR



$(^i\text{Pr})_3\text{SiH}$ (1.5 eq.)

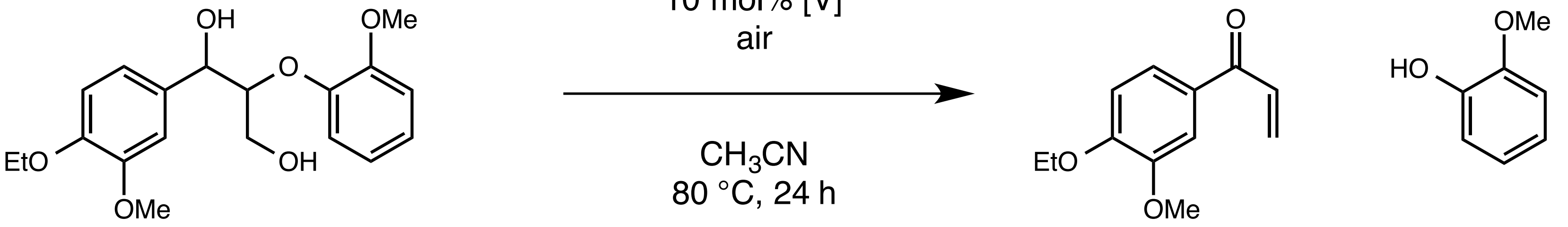
C–O cleavage conditions

89% yield

Nichols, J. M.; Bishop, L. M.; Bergman, R. G.; Ellman, J. A. *J. Am. Chem. Soc.* **2010**, *132*, 12554.

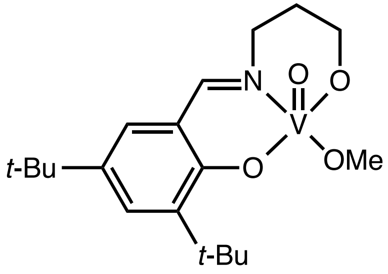
Toste's Lignin C–O Bond Cleavage with Vanadium

- Vanadium catalyst system enables non-oxidative lignin model degradation



82% yield

57% yield

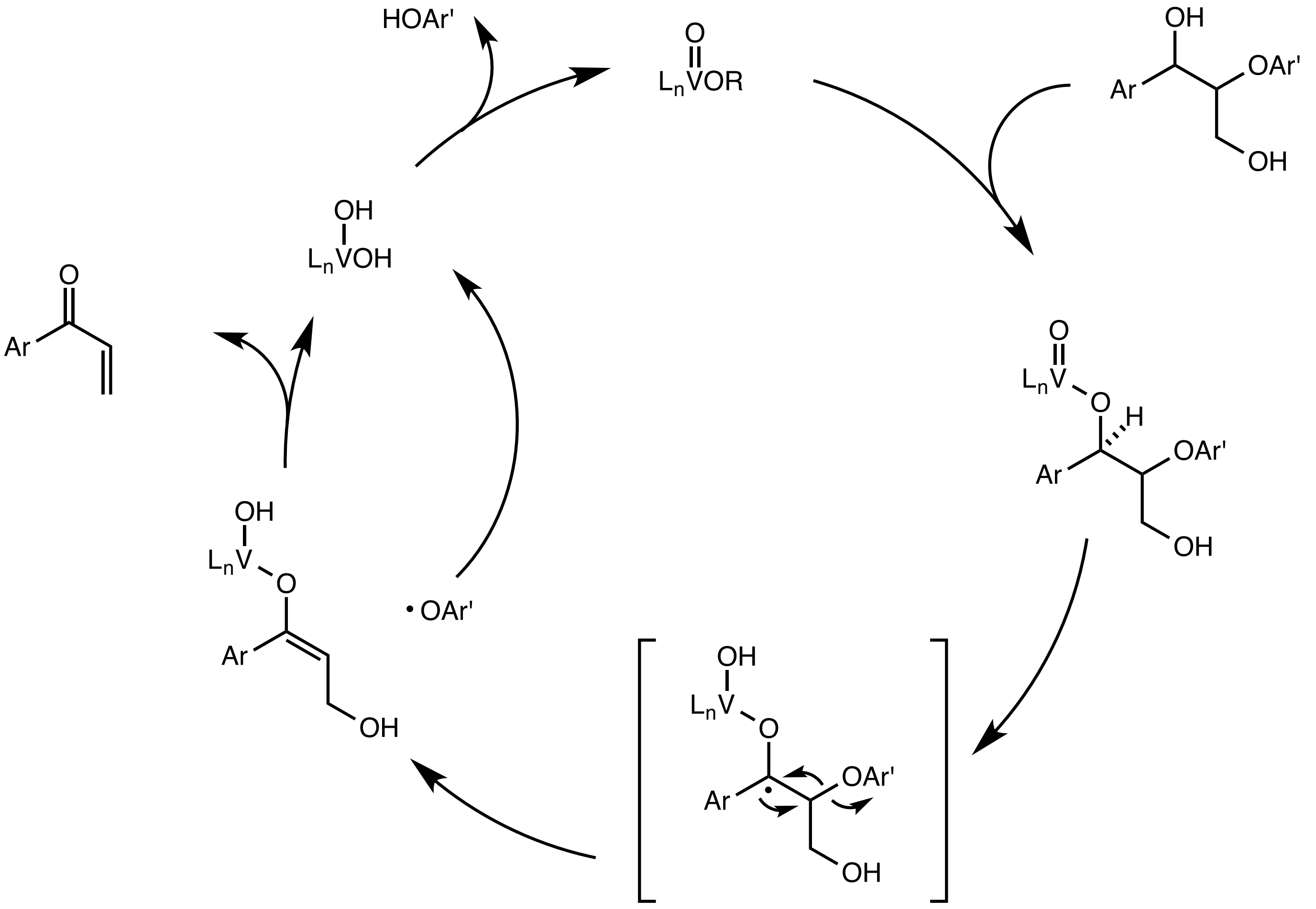


vanadium(V)-oxo catalyst

Son, S.; Toste, F. D. *Angew. Chem. Int. Ed.* **2010**, *49*, 3791.

Toste's Lignin C–O Bond Cleavage with Vanadium

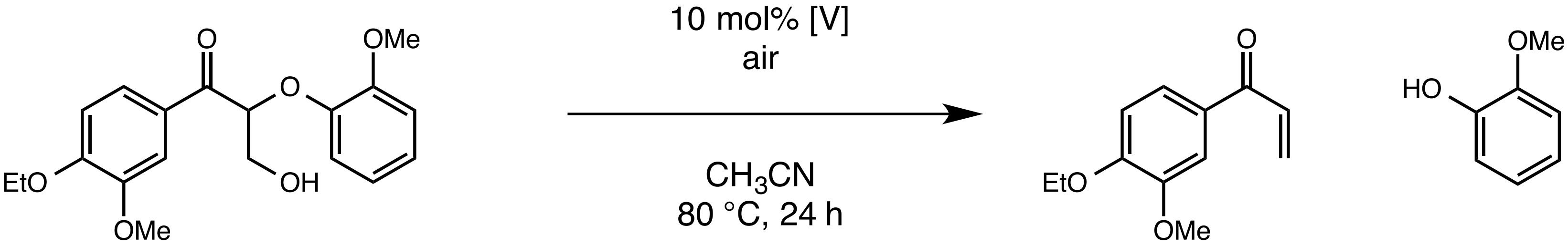
■ Proposed catalytic cycle for vanadium-catalyzed C–O bond cleavage



Son, S.; Toste, F. D. *Angew. Chem. Int. Ed.* **2010**, *49*, 3791.

Toste's Lignin C–O Bond Cleavage with Vanadium

■ Mechanistic considerations for vanadium-catalyzed C-O bond cleavage

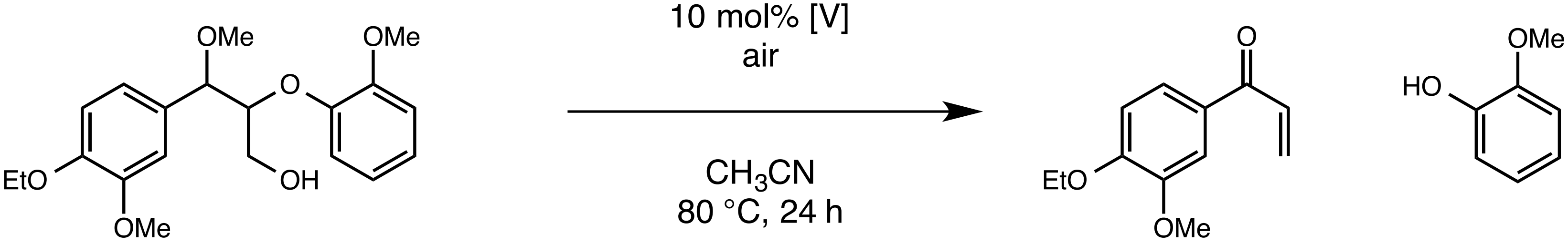


10 mol% [V]
air

CH_3CN
80 °C, 24 h

0% yield **0% yield**

84% recovery of SM



10 mol% [V]
air

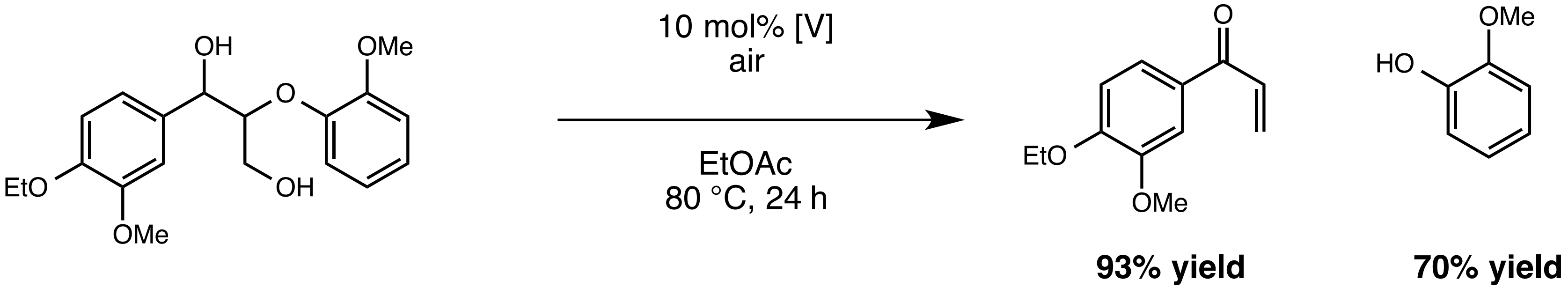
CH_3CN
80 °C, 24 h

0% yield **0% yield**

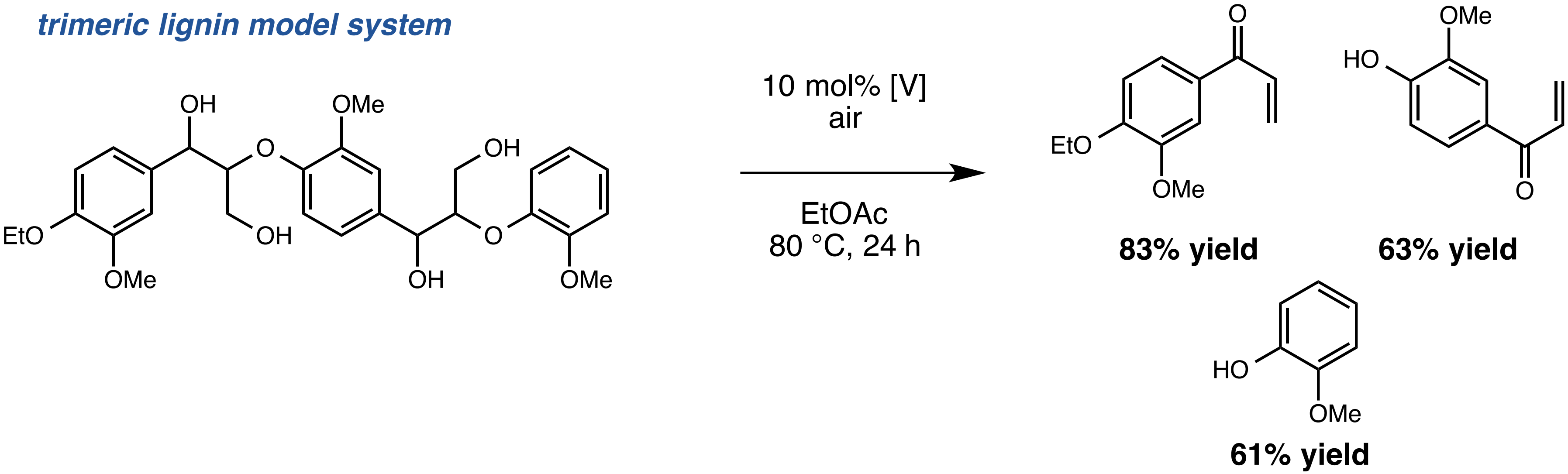
Son, S.; Toste, F. D. *Angew. Chem. Int. Ed.* **2010**, *49*, 3791.

Toste's Lignin C–O Bond Cleavage with Vanadium

- Switch to more biofuel sustainable solvent (ethyl acetate)



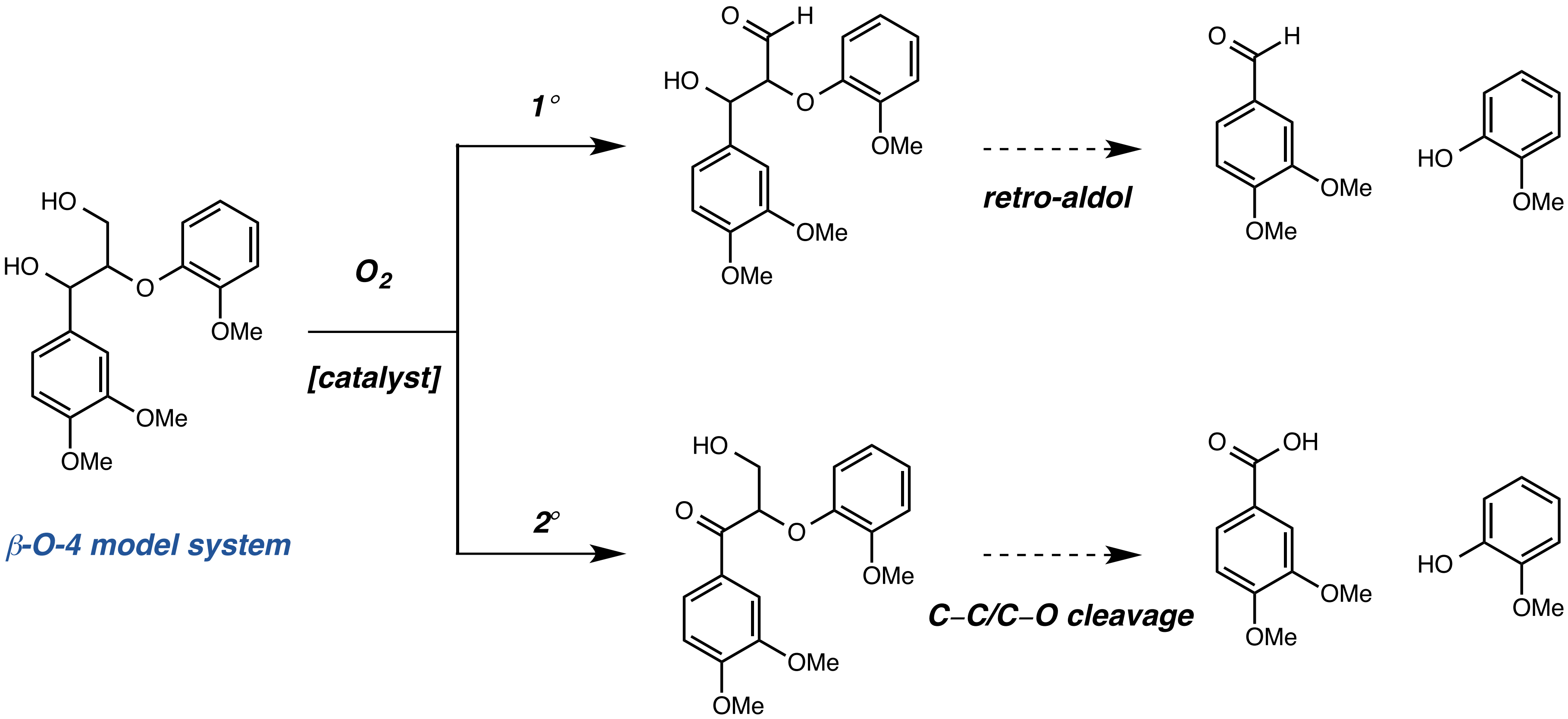
trimeric lignin model system



Son, S.; Toste, F. D. *Angew. Chem. Int. Ed.* **2010**, *49*, 3791.

Stahl's Metal-Free Aerobic Alcohol Oxidation of Lignin

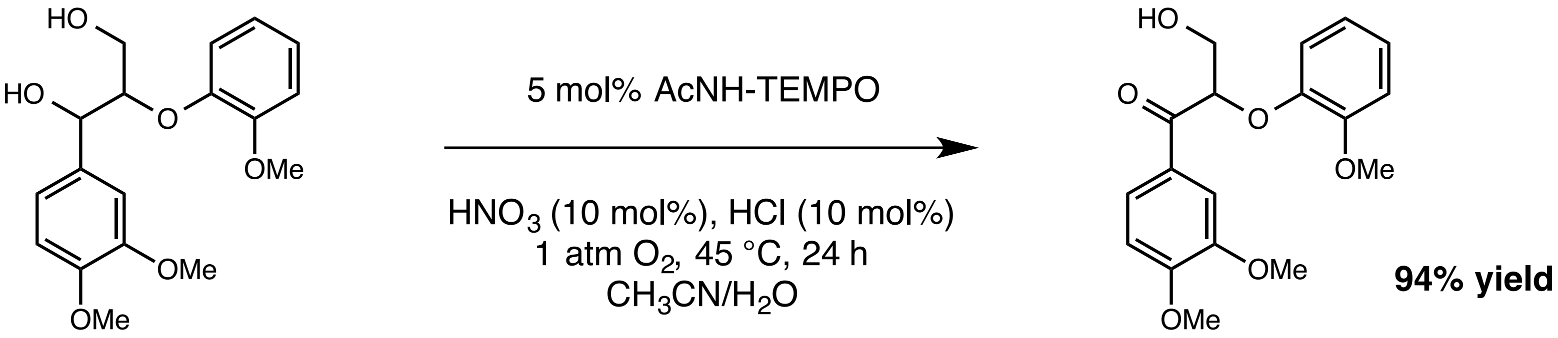
- Stahl and coworkers developed a chemoselective alcohol oxidation



Rahimi, A.; Azarpira, A.; Kim, H.; Ralph, J.; Stahl, S. S. *J. Am. Chem. Soc.* **2013**, *135*, 6415.

Stahl's Metal-Free Aerobic Alcohol Oxidation of Lignin

- TEMPO system delivers benzylic oxidation product in excellent yield and selectivity

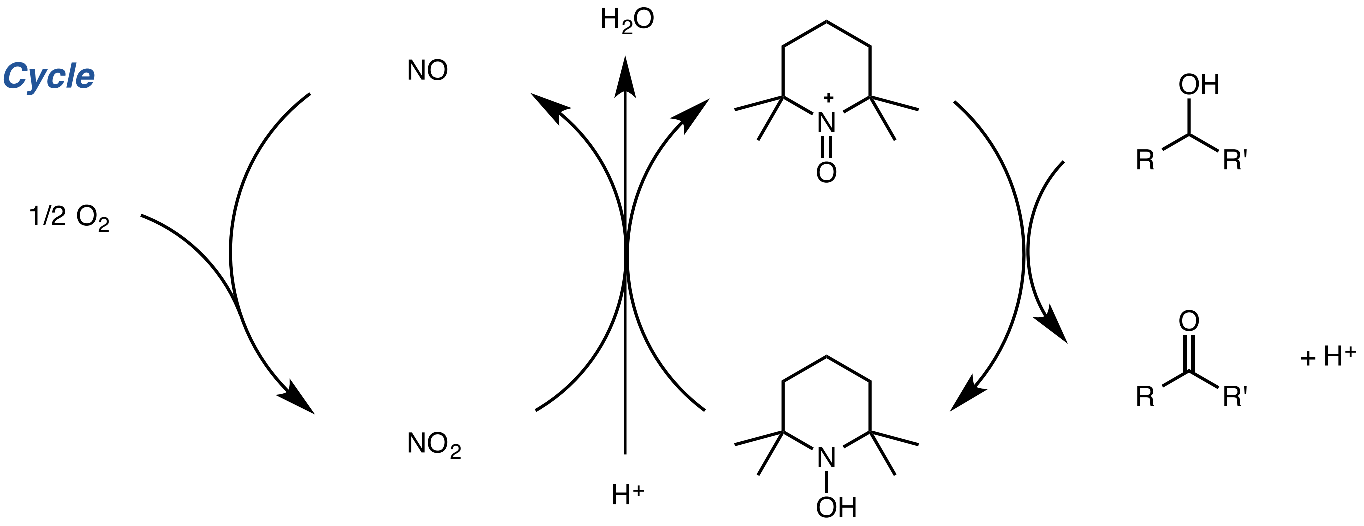


5 mol% AcNH-TEMPO

HNO_3 (10 mol%), HCl (10 mol%)
1 atm O_2, 45 °C, 24 h
CH_3CN/H_2O

94% yield

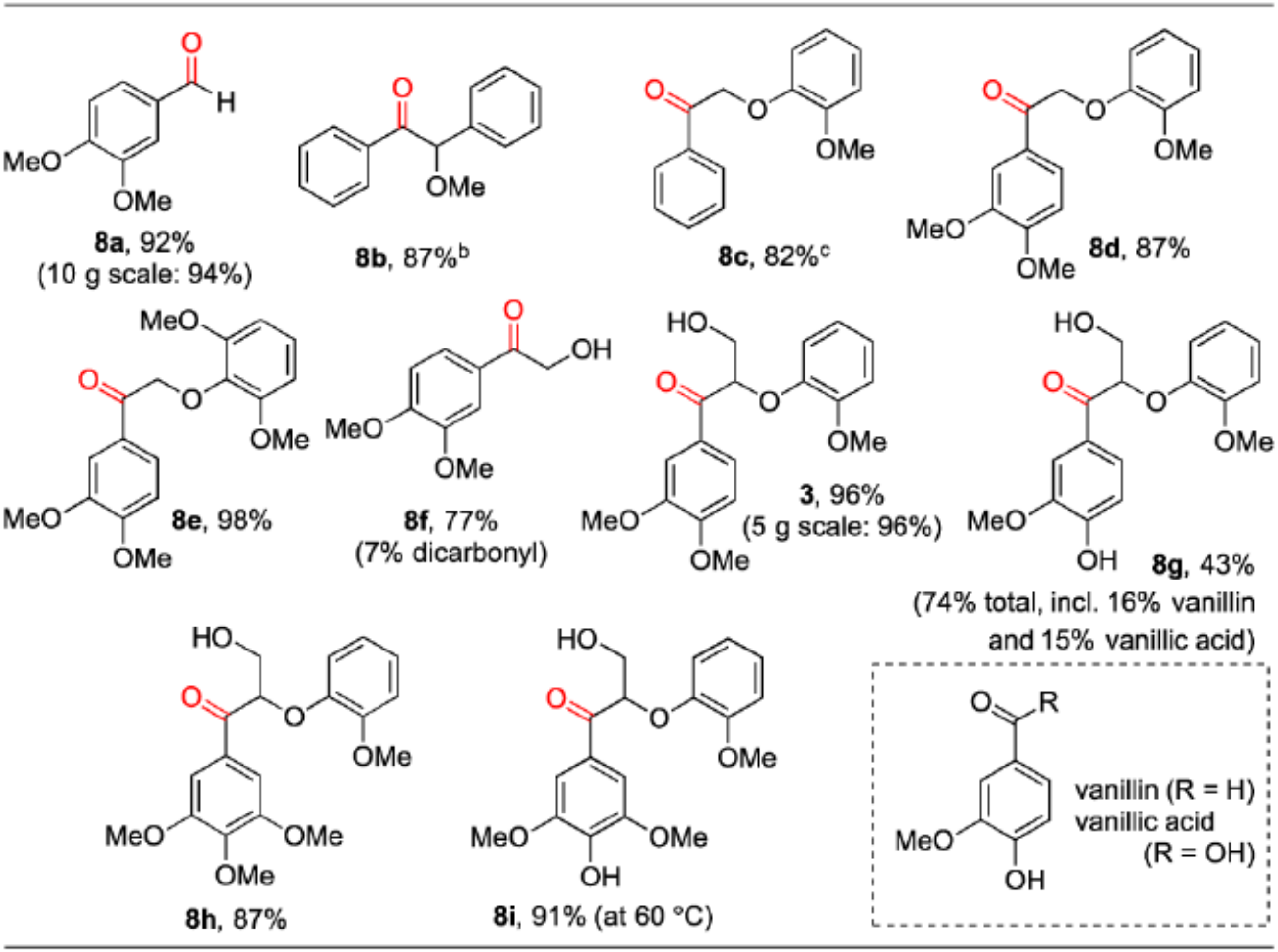
Catalytic Cycle



Rahimi, A.; Azarpira, A.; Kim, H.; Ralph, J.; Stahl, S. S. *J. Am. Chem. Soc.* **2013**, *135*, 6415.

Stahl's Metal-Free Aerobic Alcohol Oxidation of Lignin

- TEMPO benzylic oxidation is effective across a range of lignin-type systems



8a, 92%
(10 g scale: 94%)

8b, 87%[b]

8c, 82%[c]

8d, 87%

8e, 98%

8f, 77%
(7% dicarbonyl)

3, 96%
(5 g scale: 96%)

8g, 43%
(74% total, incl. 16% vanillin and 15% vanillic acid)

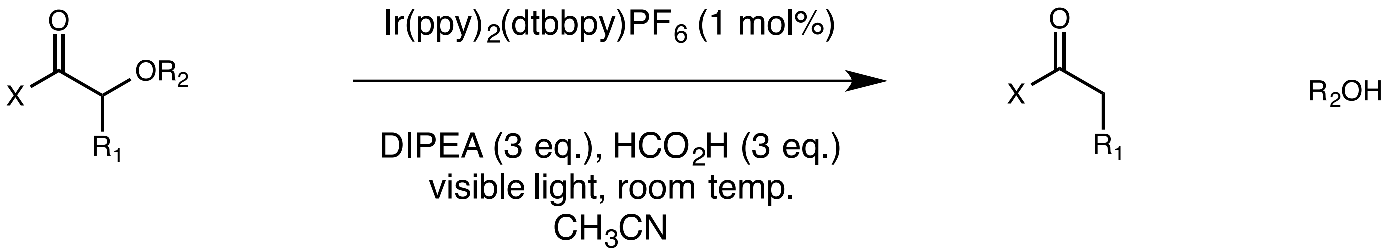
8h, 87%

8i, 91% (at 60 °C)

Rahimi, A.; Azarpira, A.; Kim, H.; Ralph, J.; Stahl, S. S. *J. Am. Chem. Soc.* **2013**, *135*, 6415.

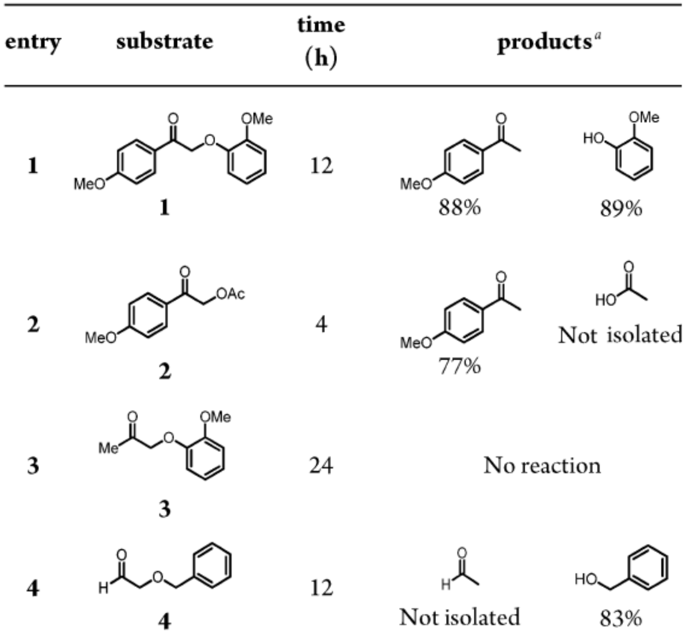
Stephenson's Photoredox Strategy for Lignin Degradation

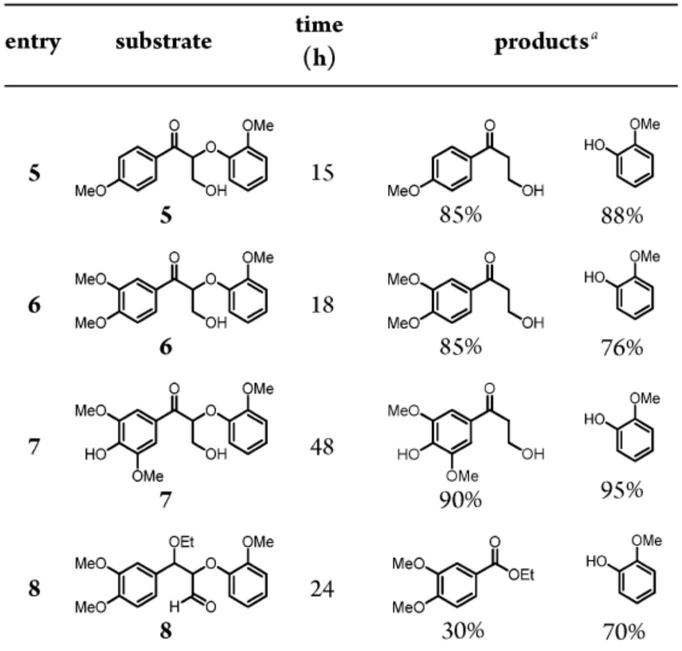
Photoredox-catalyzed C–O cleavage of α-oxy ketones



$Ir(ppy)_2(dtbbpy)PF_6$ (1 mol%)

DIPEA (3 eq.), HCO_2H (3 eq.)
visible light, room temp.
CH_3CN



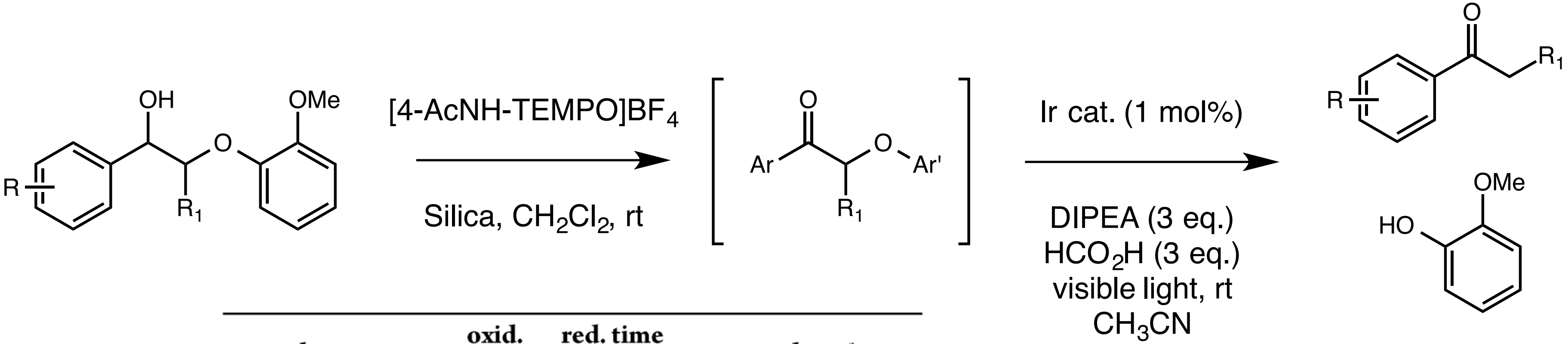


entry	substrate	time (h)	products[a]	
1	**1**	12	88%	89%
2	**2**	4	77%	Not isolated
3	**3**	24	No reaction	
4	**4**	12	Not isolated	83%
5	**5**	15	85%	88%
6	**6**	18	85%	76%
7	**7**	48	90%	95%
8	**8**	24	30%	70%

Nguyen, J. D.; Matsuura, B. S.; Stephenson, C. R. J. *J. Am. Chem. Soc.* **2014**, *136*, 1218.

Stephenson's Photoredox Strategy for Lignin Degradation

- Modified Stahl conditions enables two step oxidation/C–O bond cleavage

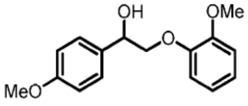
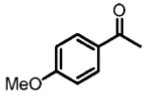
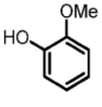
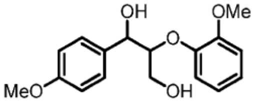
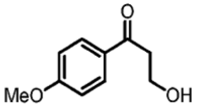
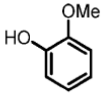
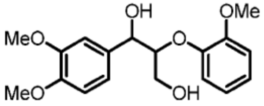
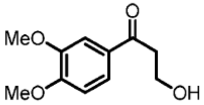
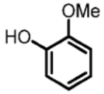


$[4\text{-AcNH-TEMPO}]BF_4$

Silica, CH_2Cl_2, rt

Ir cat. (1 mol%)

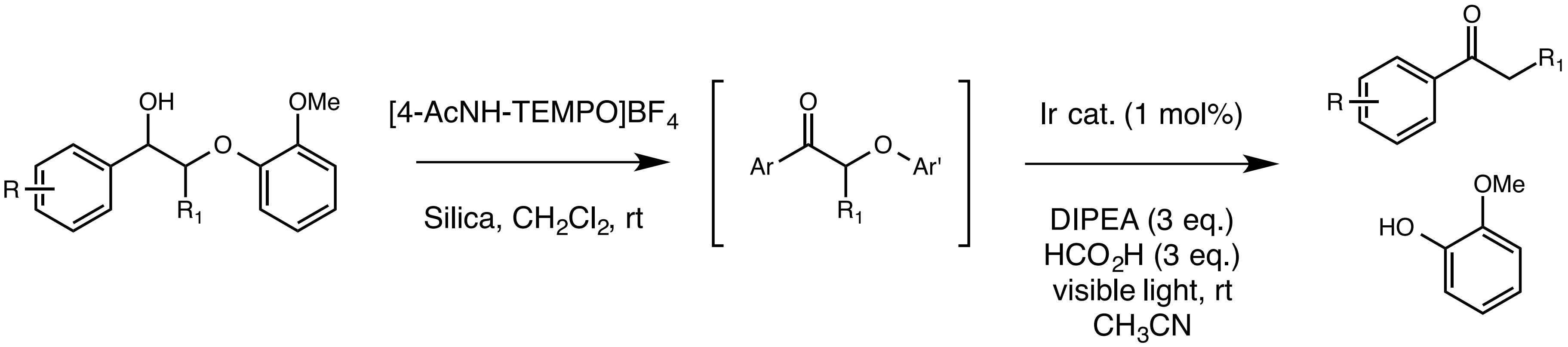
DIPEA (3 eq.)
HCO_2H (3 eq.)
visible light, rt
CH_3CN

substrate	oxid. time (h)	red. time (h)	products[a]	
 **9**	15	16	 85%	 83%
 **10**	18	20	 81%	 80%
 **11**	15	14	 84%	 93%

Nguyen, J. D.; Matsuura, B. S.; Stephenson, C. R. J. *J. Am. Chem. Soc.* **2014**, *136*, 1218.

Stephenson's Photoredox Strategy for Lignin Degradation

- Modified Stahl conditions enables two step oxidation/C–O bond cleavage



- Reaction can be performed in flow to decrease reaction times (20 h to 33 min, >90% yield)

Reaction proceeds in presence of lignosulfonate additive to replicate irradiating dark solutions

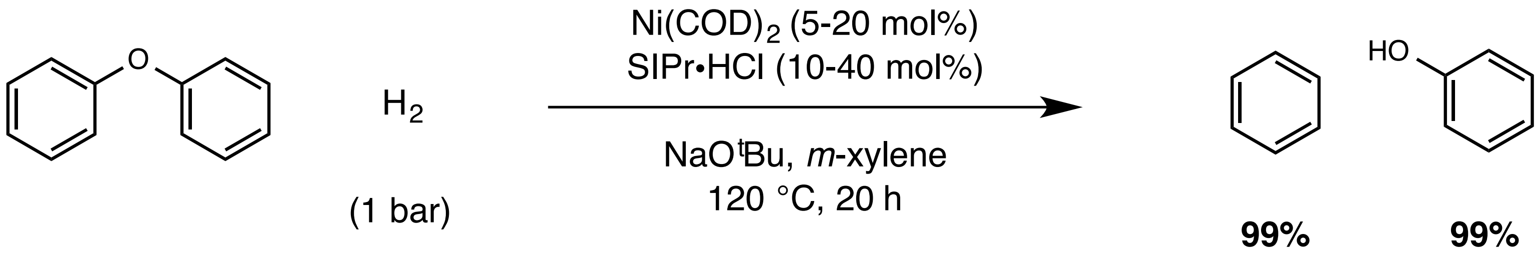
batch = 0% yield
flow = 90% yield

Reaction Mixture

Nguyen, J. D.; Matsuura, B. S.; Stephenson, C. R. J. *J. Am. Chem. Soc.* **2014**, *136*, 1218.

Hartwig's Nickel-Catalyzed Aromatic C–O Cleavage

- Hartwig and coworkers have developed a method to cleave aryl ethers with H_2

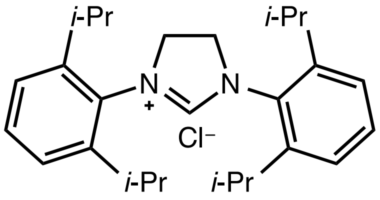


H_2 (1 bar)

$Ni(COD)_2$ (5-20 mol%)
SIPr•HCl (10-40 mol%)

NaO^tBu, *m*-xylene
120 °C, 20 h

99% **99%**



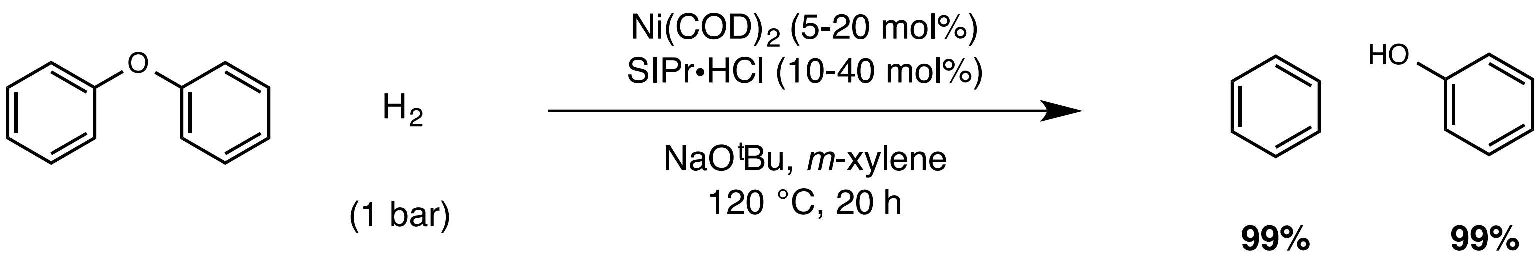
SIPr•HCl

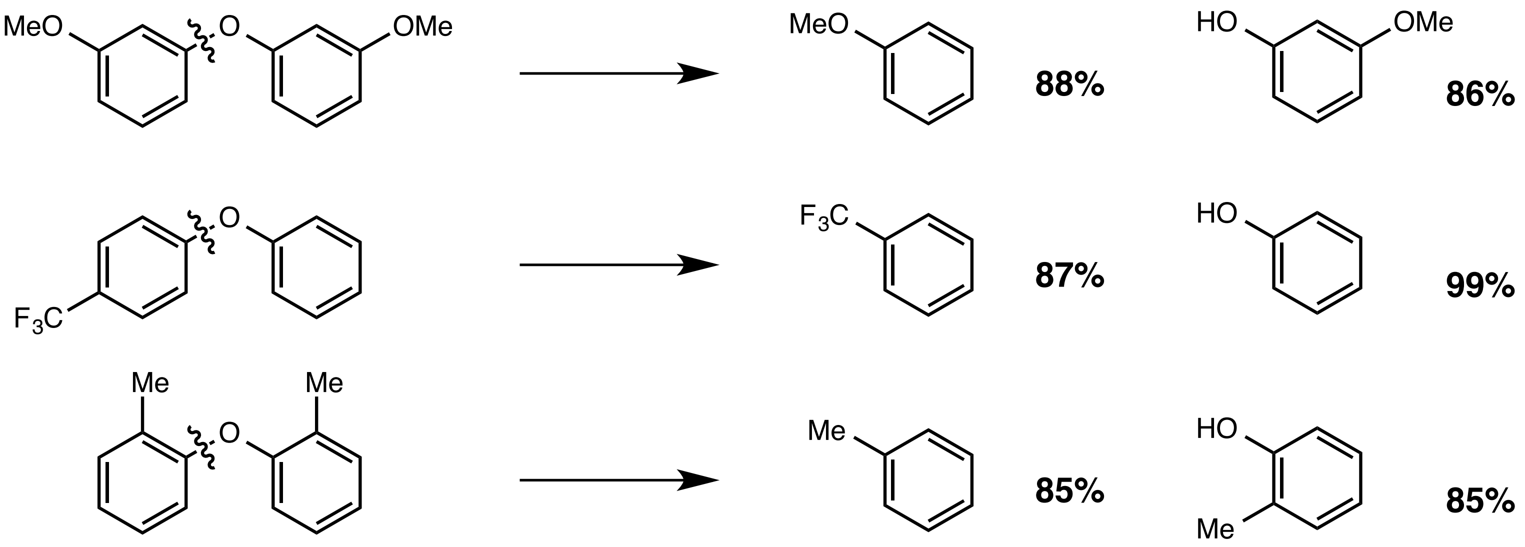
Other reducing agents effect the transformation (DIBAL, LAH, silanes) - H_2 is cheaper, cleaner, milder reagent

Sergeev, A. G.; Hartwig, J. F. *Science* **2011**, *332*, 439.

Hartwig's Nickel-Catalyzed Aromatic C–O Cleavage

- Hartwig and coworkers have developed a method to cleave aryl ethers with H_2



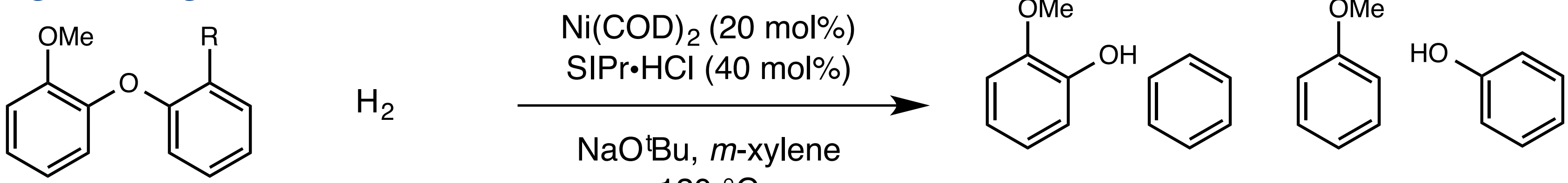


Sergeev, A. G.; Hartwig, J. F. *Science* **2011**, *332*, 439.

Hartwig's Nickel-Catalyzed Aromatic C–O Cleavage

■ Lignin model systems show selective cleavage of aryl ether bonds

4-O-5 lignin linkage



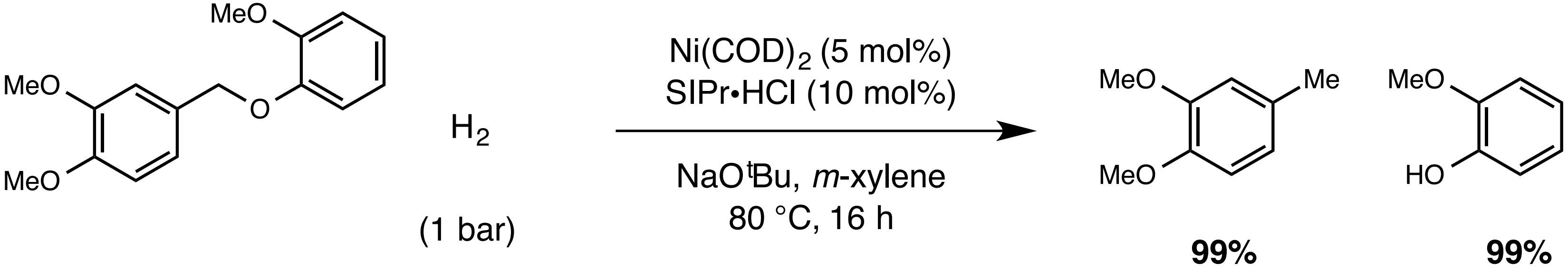
H_2 (1 bar)

Ni(COD)$_2$ (20 mol%)
SIPr•HCl (40 mol%)

NaO^{t}Bu, *m*-xylene
120 °C

R=OMe	**66%**	**15%**	**47%**	**-**
R=H	**68%**	**63%**	**19%**	**22%**

α-O-4 lignin linkage



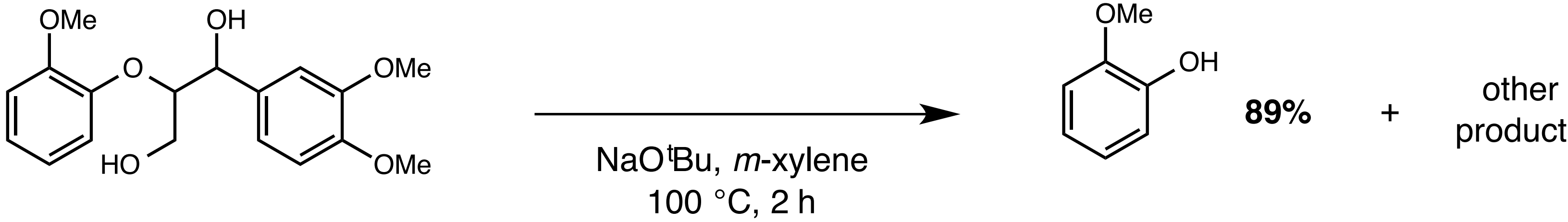
H_2 (1 bar)

Ni(COD)$_2$ (5 mol%)
SIPr•HCl (10 mol%)

NaO^{t}Bu, *m*-xylene
80 °C, 16 h

99% **99%**

β-O-4 lignin linkage

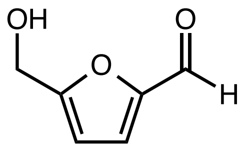


NaO^{t}Bu, *m*-xylene
100 °C, 2 h

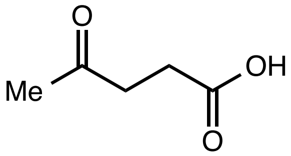
89% + other products

Sergeev, A. G.; Hartwig, J. F. *Science* **2011**, *332*, 439.

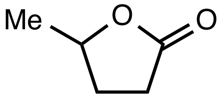
Platform Chemicals and Upgrading Strategies



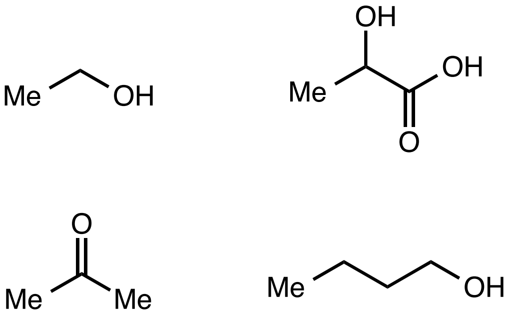
5-hydroxymethylfurfural (HMF)



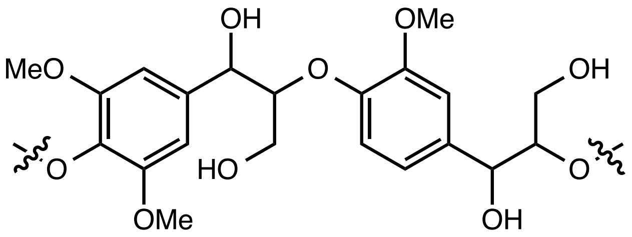
levulinic acid (LA)



γ-valerolactone (GVL)



fermentation products



lignin

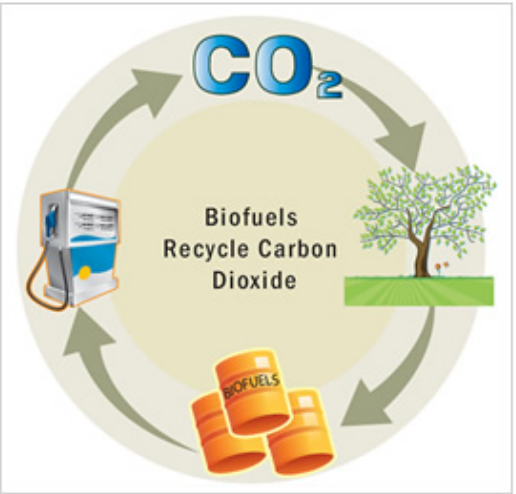
The Future of Biofuels

- Utilizing biomass as a renewable resource for biofuel production has a lot of potential

abundant feedstocks

carbon neutral

uses pre-existing infrastructure



- Despite advances, engineers and chemists must collaborate to:

1) Continue to develop robust strategies to product platform chemicals
2) Discover novel applications for platform chemicals via upgrading
3) Establish integrated methods, with facile separation and purification processes

Untapped potential for chemists to apply knowledge of catalysis to enable milder methods

Alonso, D. M.; Bond, J. Q.; Dumesic, J. A. *Green Chem.* **2010**, *12*, 1493.