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Engineering

# CHALLENGES IN MODELING EARLY STAGE TRANSPORT FUEL TECHNOLOGY

Process understanding for prospective LCA

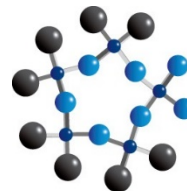
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**CRC WORKSHOP, ARGONNE NATIONAL LABORATORY, OCT 2017**



**Pacific Northwest**  
NATIONAL LABORATORY



**CERAMATEC®**  
TOMORROW'S CERAMIC SYSTEMS



# Background:

- Energy policy incentivizing the development of renewable/low carbon fuels in the US:
  - Policy incentivizing R&D of “drop-in” fuels
  - LCA is used to measure the environmental performance of new transport fuels under development
  - TEA is used to measure economic metrics
- Major Challenges *and* CRC Workshop Goals:
  - Lack of data; uncertainty; unknowns; policy actions
- Multiple Product System:
  - Fuels, chemicals, materials
  - The need for **Prospective LCA**

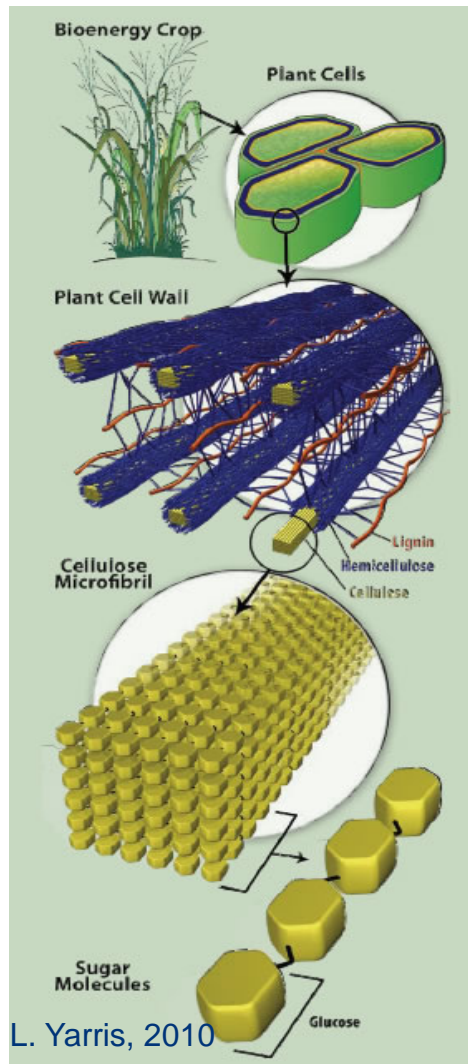


# LCA/TEA for early-stage technology

- Two challenges when undertaking environmental and economic evaluation of new technology
  - Building life cycle assessment (LCA) models in the absence of data: thermodynamic
  - Estimating cost of investing in new technology



# Pathways for Converting Biomass



## Bio-molecular

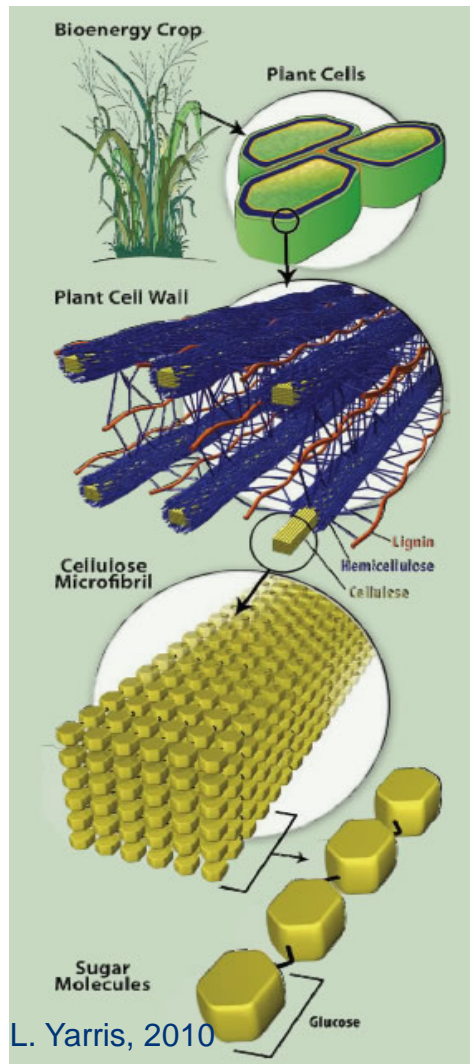
- Fermentation of sugars

## Thermo-Chemical

- Combustion
- Gasification
- Slow and Fast Pyrolysis

- Fuels (energy)
- Chemicals
- Materials

# Pathways for Converting Biomass



## Bio-molecular

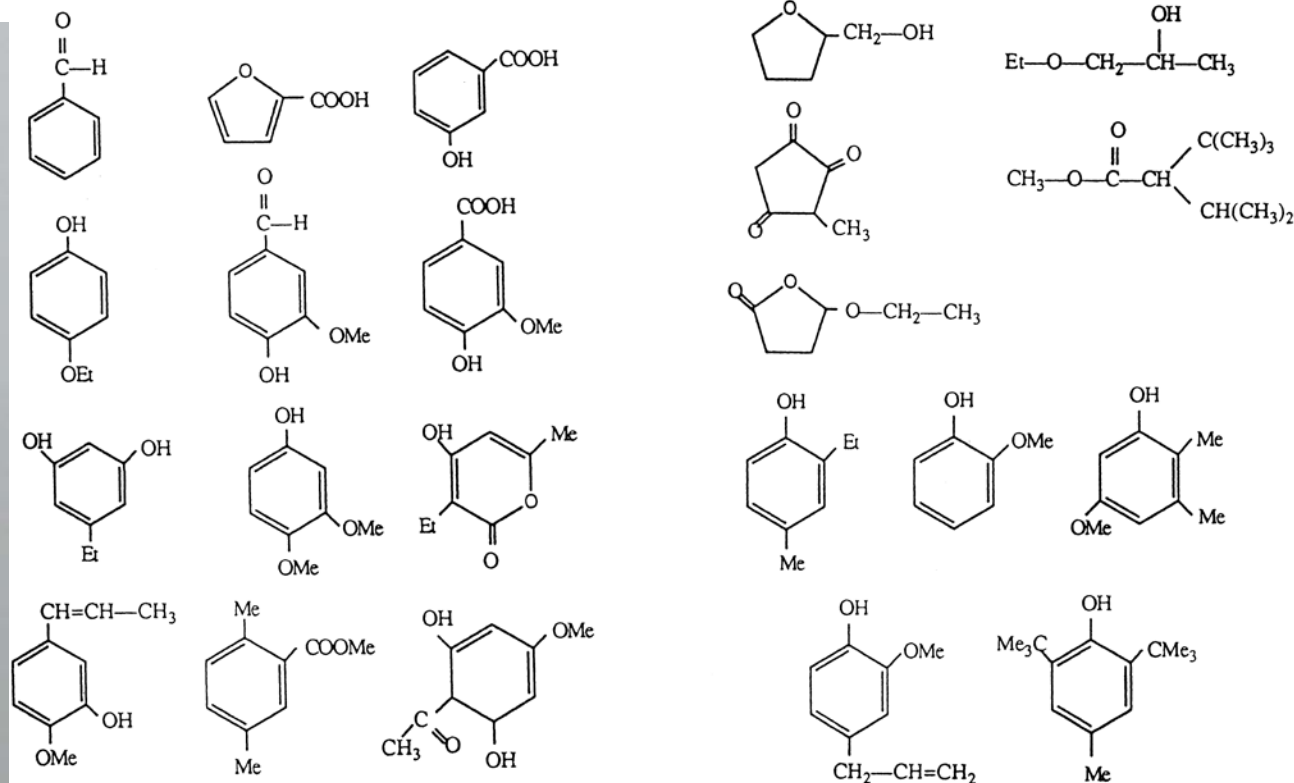
- Fermentation of sugars

## Thermo-Chemical

- Combustion
- Gasification
- Slow and **Fast Pyrolysis**

- **Fuels (energy)**
- **Chemicals**
- Materials

# BIO-OIL CRUDE

Zhang et al. *Scientific Reports* 2013: **3**, 1120

Furimsky, E. *Applied Catalysis A: General* 2000;**199**,147–190



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INTRODUCTION | DEOX | ELECTRO DEOX | DFT | IMPLICATIONS | 6

## BIO-OIL CRUDE



Zhang et al. *Scientific Reports* 2013: **3**, 1120

Characteristic	Fast pyrolysis Bio-oil Wet ----- Dry		Heavy petroleum fuel
Water content, wt%	15-25		0.1
Insoluble solids, %	0.5-0.8		0.01%
Carbon, %	39.5	55.8	85.2
Hydrogen, %	7.5	6.1	11.1
Oxygen, %	52.6	37.9	1.0
H/C	2.3	1.3	1.6
O/C	1.0	0.5	0.01
Nitrogen, %	<0.1		0.3
Sulfur, %	<0.05		2.3
Ash	0.2-0.3		<0.1
HHV, MJ/kg	17		40
Density, g/ml	1.23		0.94
Viscosity, cp	10-150@50°C		180@50°C

D. Elliott, PNNL, 2014.

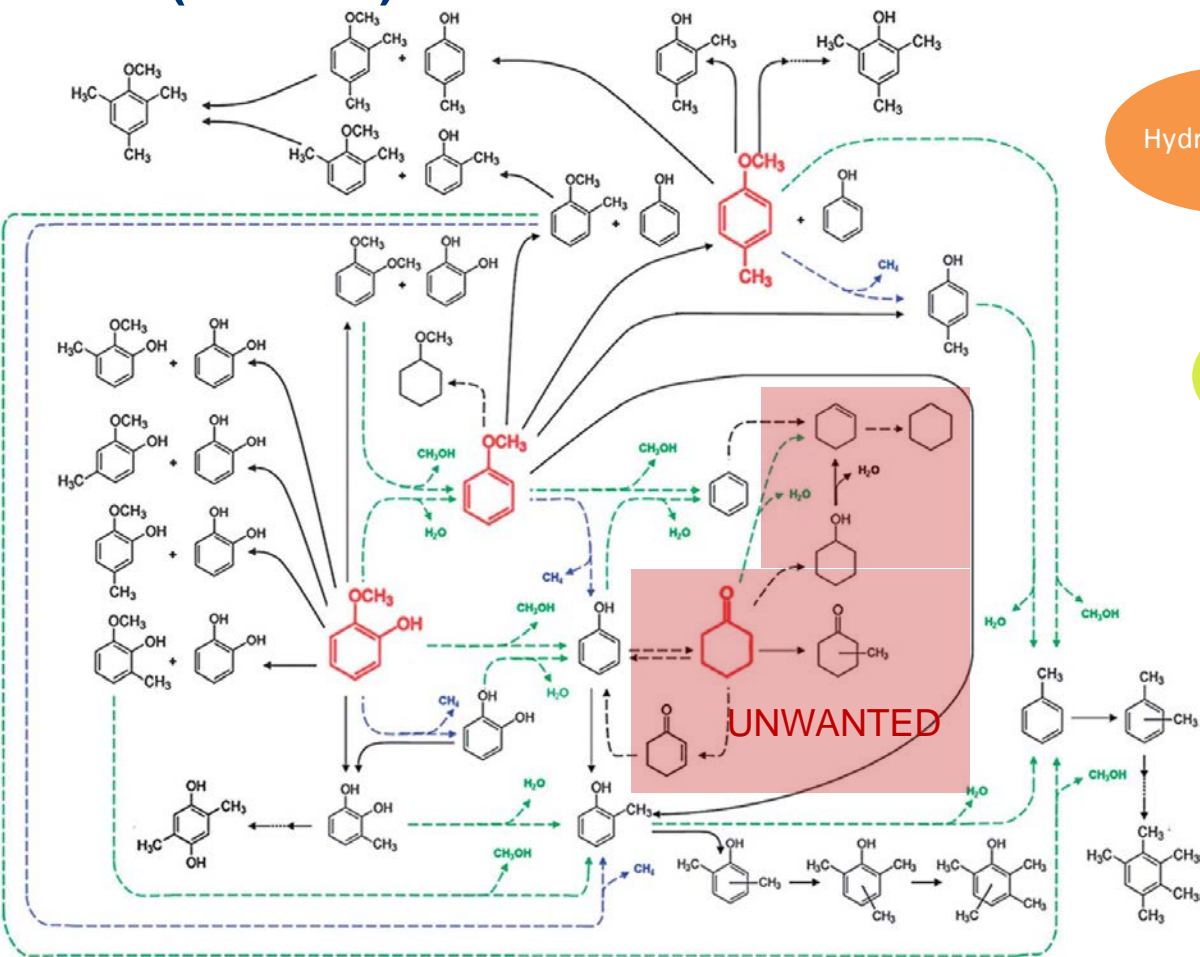
Acidic  
Viscous  
Reactive  
Corrosive



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# (HYDRO)DEOXYGENATION



Saidi et al. *Energy & Environ Sci* 2014: 7(1), 103-29



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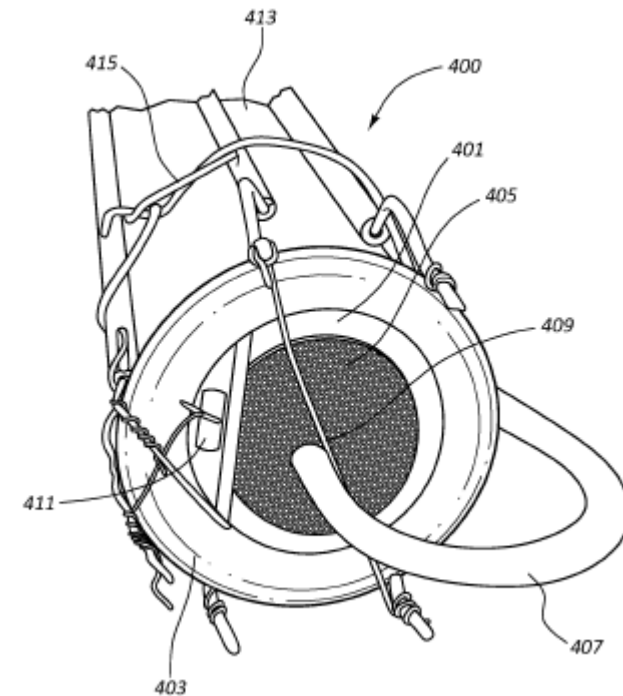
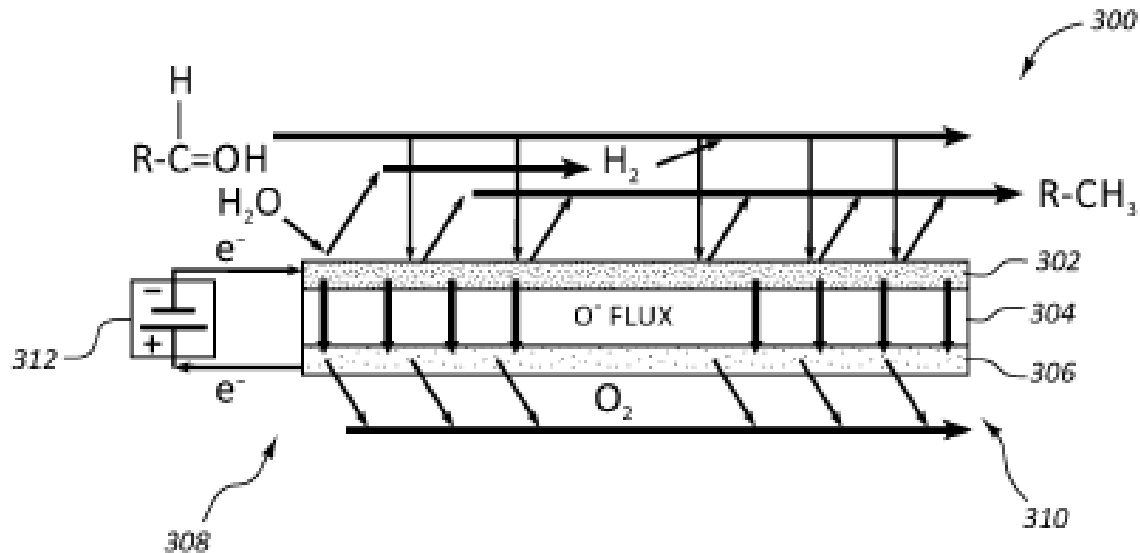
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# Pyrolysis Oil Upgrading

- (Hydro)deoxygenation (HDO), TEA (Jones et al.)
- LCA studies:
  - Hsu, 2012
  - Zhang, 2013
- Other means of upgrading:
  - Improved deoxygenation at the pyrolysis stage + mild hydrotreating
    - Catalytic pyrolysis; Tail gas reactive pyrolysis; others
  - Electrochemical deoxygenation (EDOx)



# ELECTROCHEMICAL DEOXYGENATION

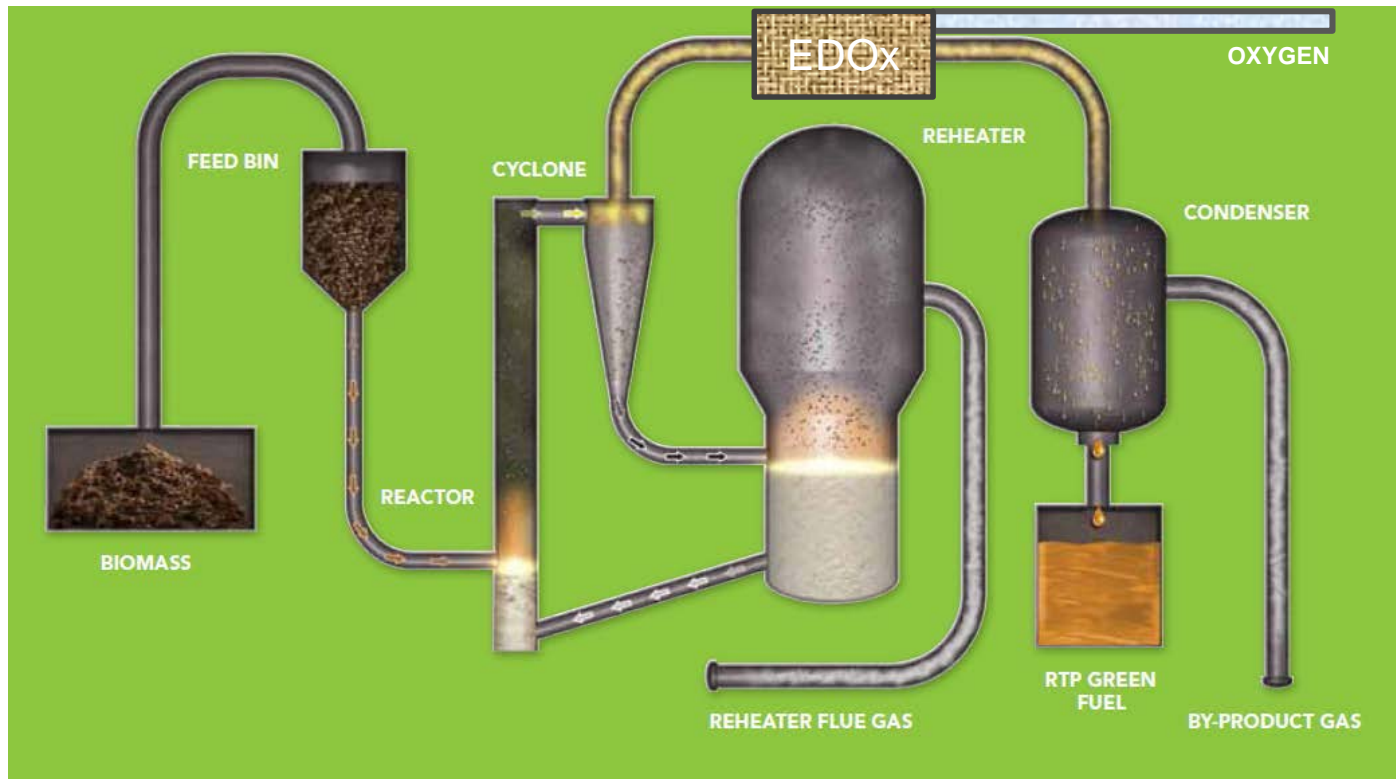


- In-situ generation of H<sub>2</sub> by electrolysis of bio-oil water (cathode)
- Deoxygenation of bio-oil at catalytic membrane by H<sub>2</sub> (cathode)
- O<sup>2-</sup> transport to ceramic, catalytic membrane, resulting in pure O<sub>2</sub> flow (anode)

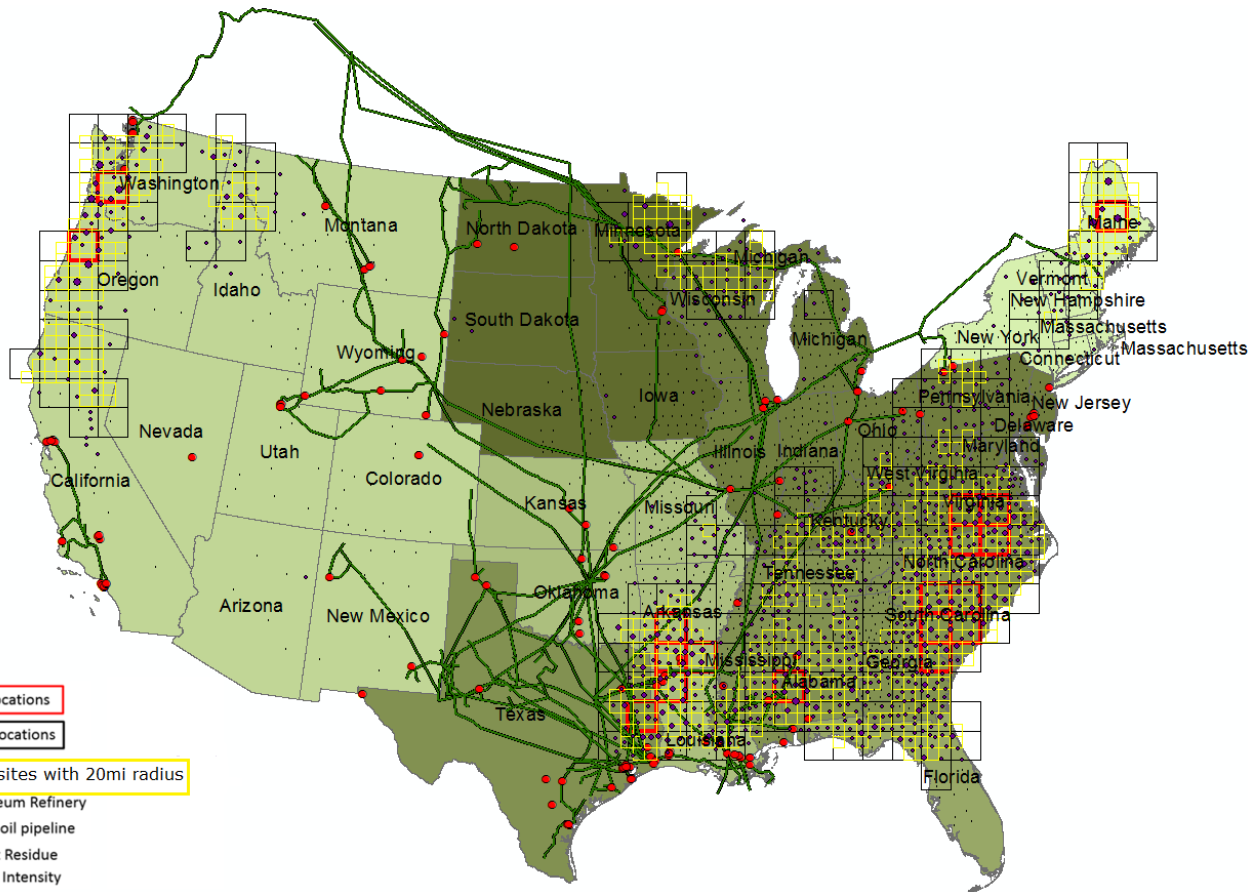


# ELECTROCHEMICAL DEOXYGENATION

- Process integration, no reheating + no external  $H_2$



# Stable pyrolysis oils can serve as densification hubs for biorefineries



- EDOX (300MTPD) and HDO (2000MTPD) locations
- Forest residue available within <20mi radius of EDOx facility proposed locations
- EDOx locations near petroleum refineries (red dot) show opportunity for improving intermediate product transport/logistics in relation to final upgrading

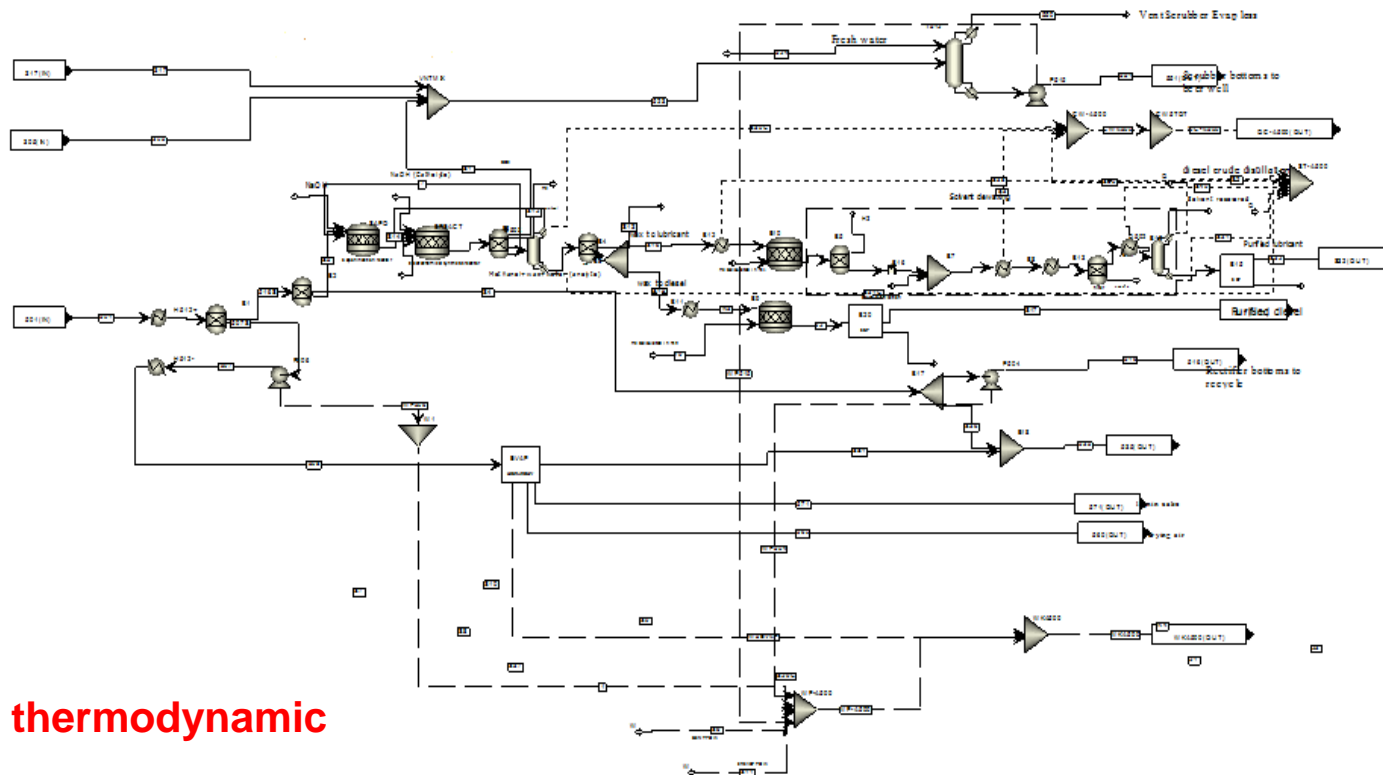
Sorunmu et al. 2017



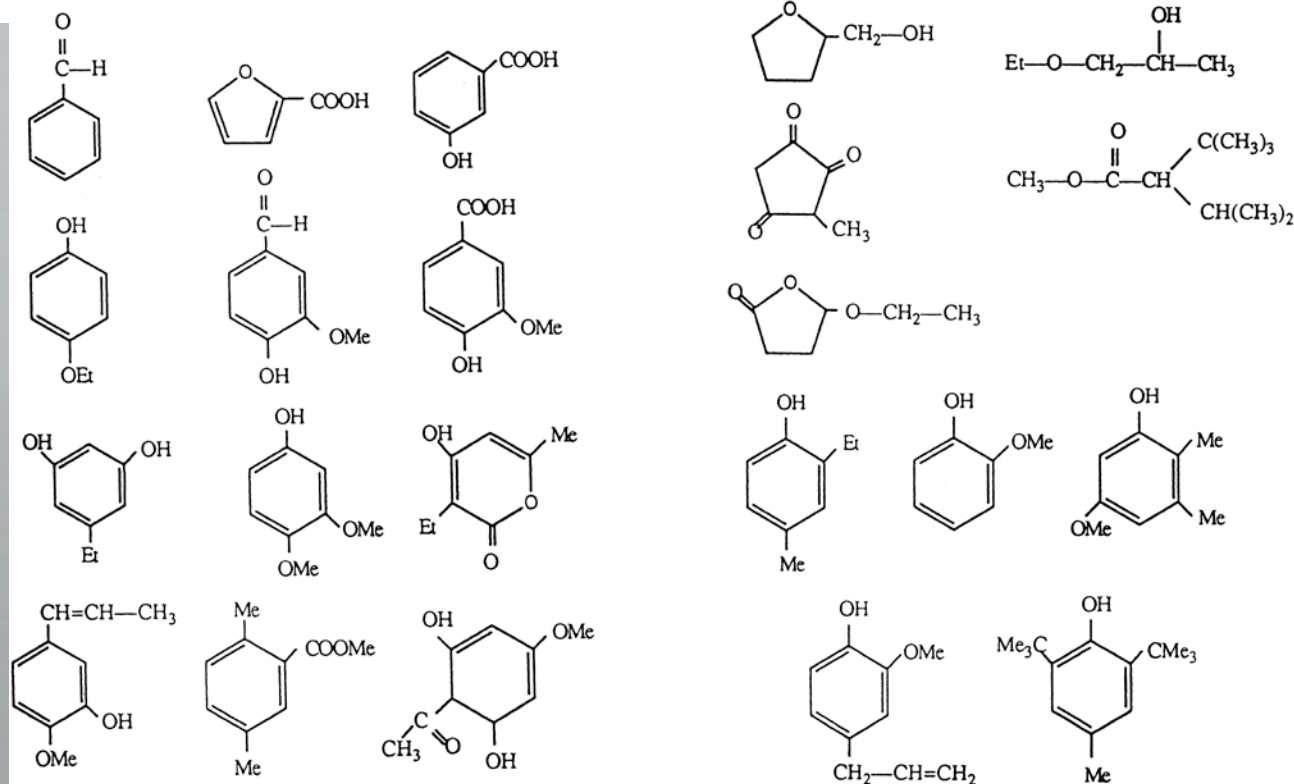
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# Building LCI's without commercial data

- Usual tools and databases: GREET, GHGenius, Ecoinvent,.. lack of data
- Simulate data from bottom-up: chemical process modeling and simulation (Aspen Plus, Superpro, FactSage)



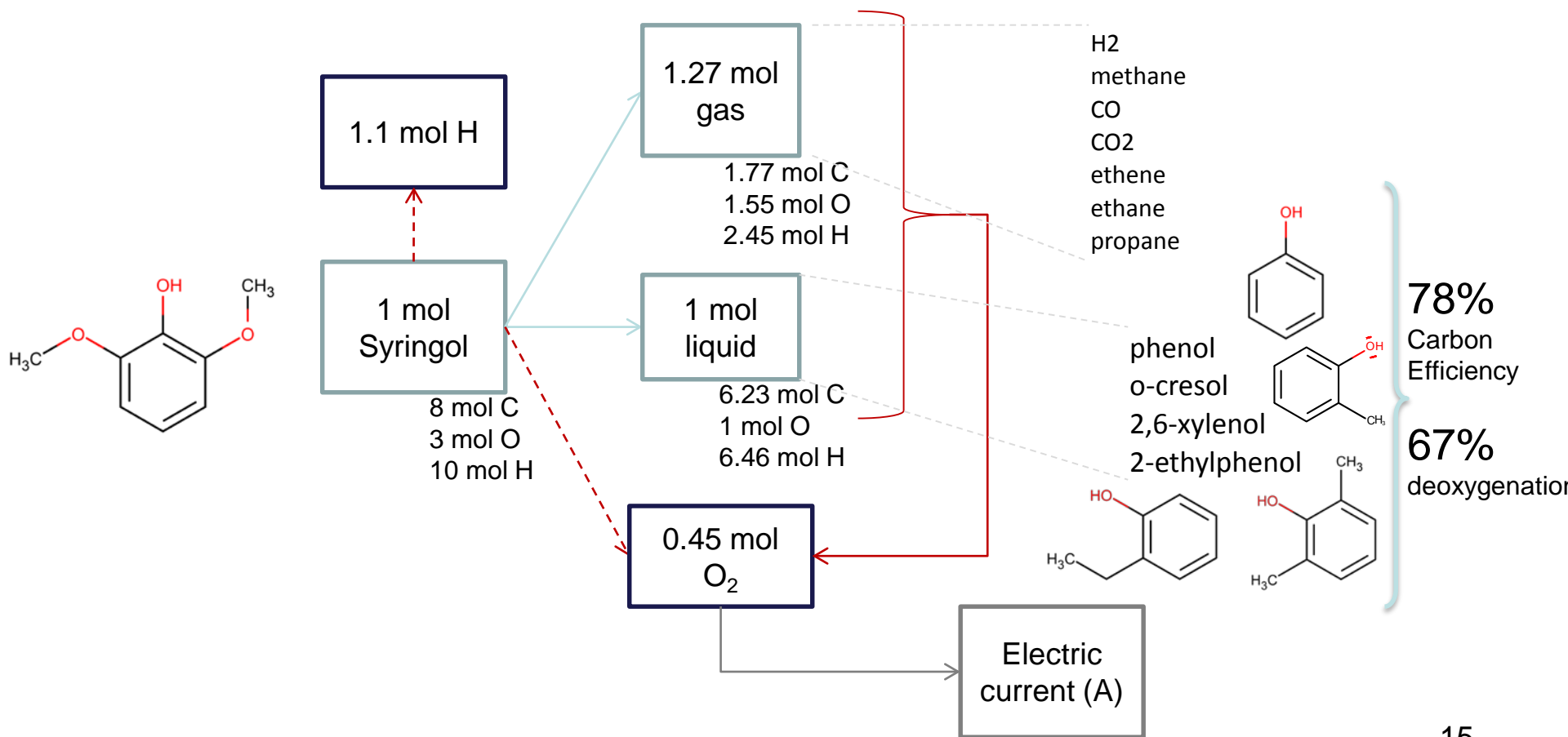
**Lack of thermodynamic data!**



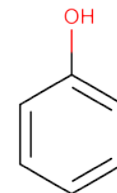
Furimsky, E. *Applied Catalysis A: General* 2000;**199**,147–190

# Work with bottom-up data

## MODEL COMPOUND: SYRINGOL



# ENERGY BALANCE



- Calculation methods

- Reaction Enthalpy

- Via Enthalpies of Formation

$$\Delta H_r = \sum H_f(\text{prod}) - \sum H_f(\text{react})$$

$H_f$  from NIST Chemistry Webbook

No  $C_p$  for many molecules

Quantity	Value	Units	Method	Reference
$\Delta_f H^\circ_{\text{gas}}$	$-96.36 \pm 0.59$	kJ/mol	Ccb	Cox, 1961
$\Delta_f H^\circ_{\text{gas}}$	$-96.44 \pm 0.63$	kJ/mol	Ccb	Andon, Biddiscombe, et al., 1960
$\Delta_f H^\circ_{\text{gas}}$	-94.2	kJ/mol	N/A	Parks, Manchester, et al., 1954
$\Delta_f H^\circ_{\text{gas}}$	-95.3	kJ/mol	N/A	Badoche, 1941

- Via Bond Dissociation Energies

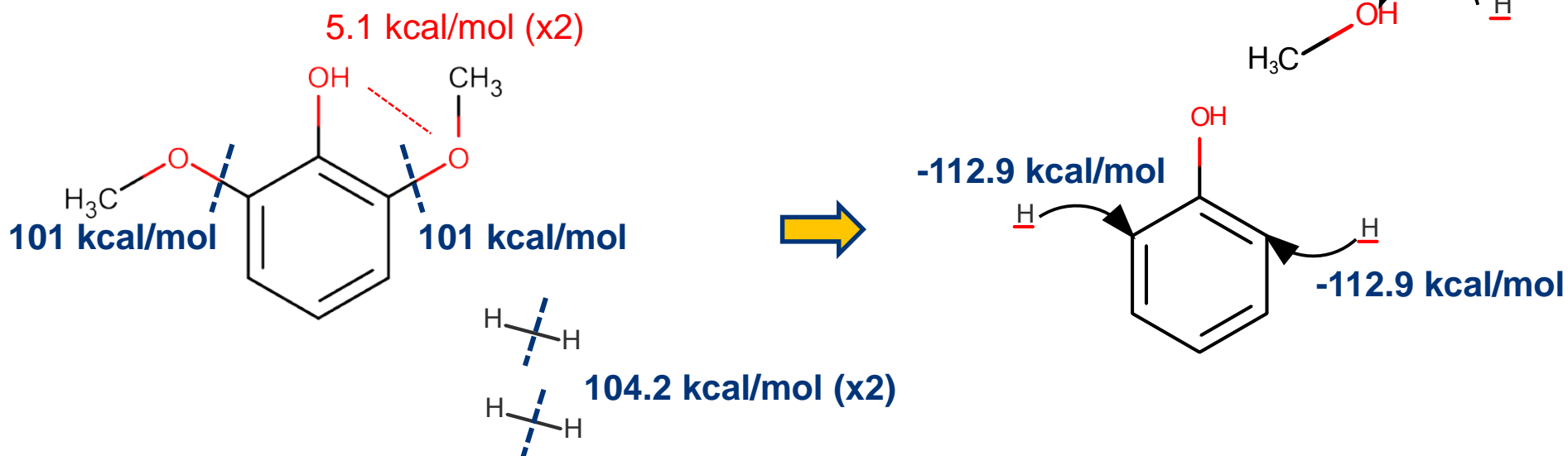
$$\Delta H_r = \sum \text{BDE}(\text{bonds formed}) - \sum \text{BDE}(\text{bonds broken})$$

Data from e.g. Blanksby and Ellison 2003, Ruscic 2015

- Gibbs Free Energy

Data on  $S_f$ ,  $C_p$  too limited

# BOND DISSOCIATION ENERGY



Bond dissociation energies give an idea about reaction sequence

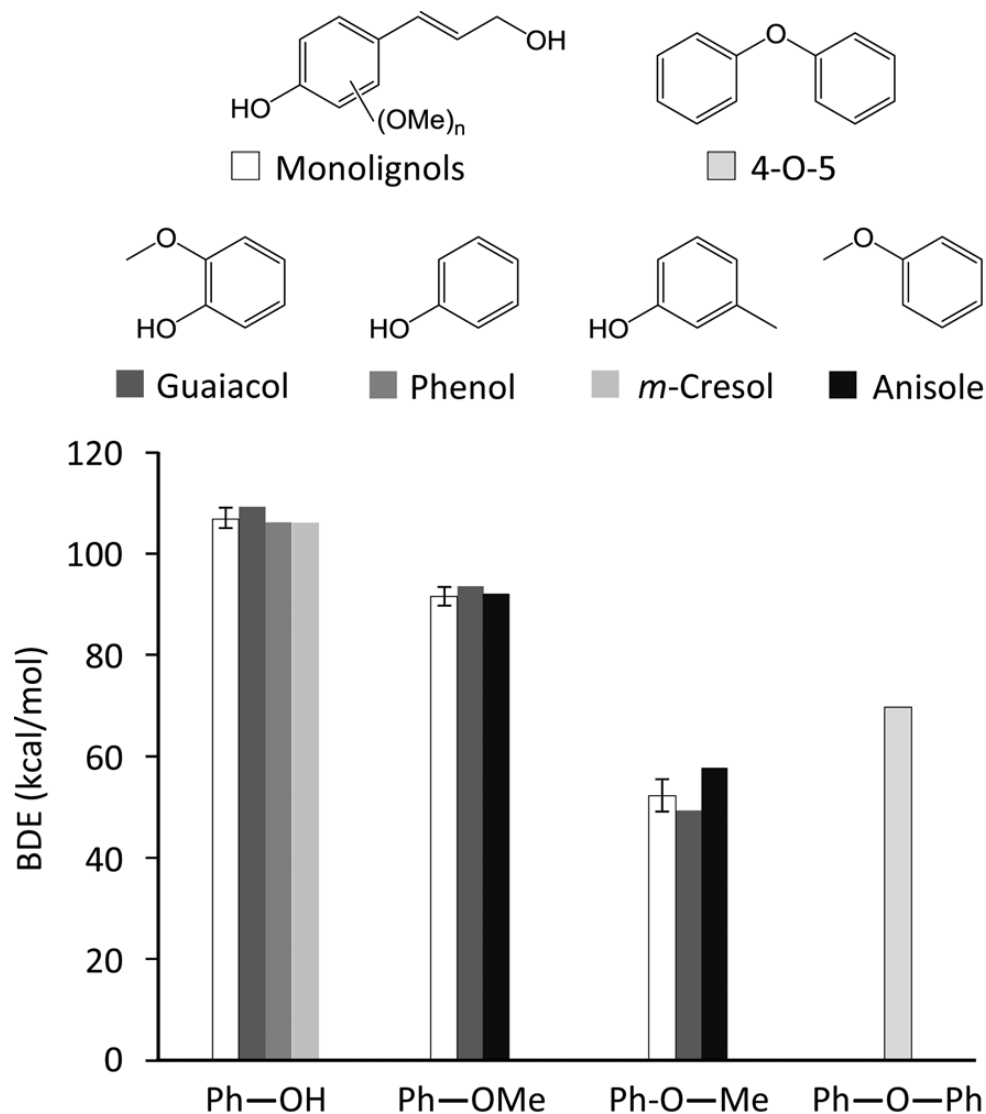
Bond dissociation energies (kJ/mol)

RO-R	339
RO-Ar	422
R-OH	385
Ar-OH	468

Furimsky, E. *Applied Catalysis A: General* 2000:**199**,147–190

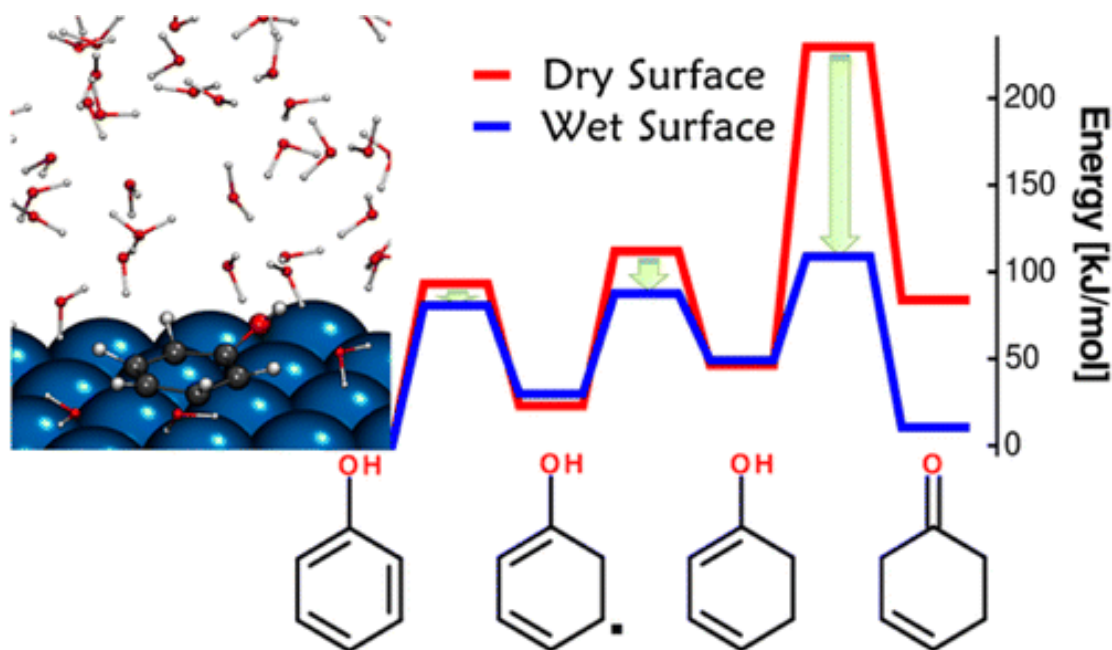
# BOND DISSOCIATION ENERGY

- BDE of functional groups dependent on other functional groups ( $\pm$ )
- Generalizable calculation strategy (overcome lacking formation enthalpy data)



# Density Functional Theory (DFT)

Computational quantum mechanical modelling method to investigate the electronic structure (principally the ground state) of atoms, molecules, and condensed phases

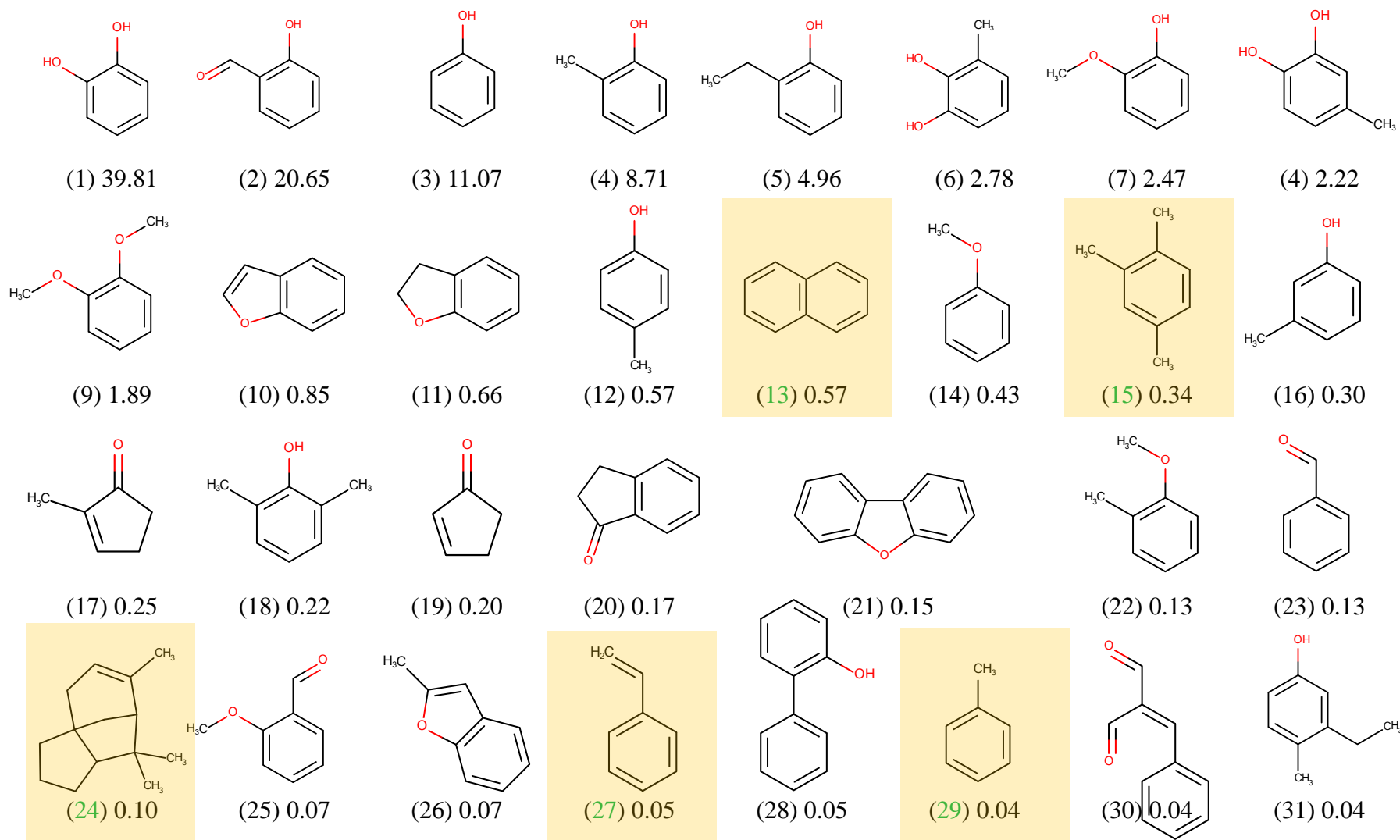


Prospective LCA:

Yoon , Y., et al. J. Am. Chem. Soc. 2014, 136, 10287–10298

1. Prediction of reaction pathways, e.g. projection of upgraded oil products  
→ Yields required operating conditions and utilities (H<sub>2</sub>) consumption
2. Prediction of thermodynamic data, e.g. G, for compounds involved  
→ Yields energy balances (of known reactions/conversions)

## 9.6 V electrochemical deoxygenation of guaiacol in a 6-cell membrane stack at 550 °C



# Ni-CATALYZED (HYDRO)DEOXYGENATION

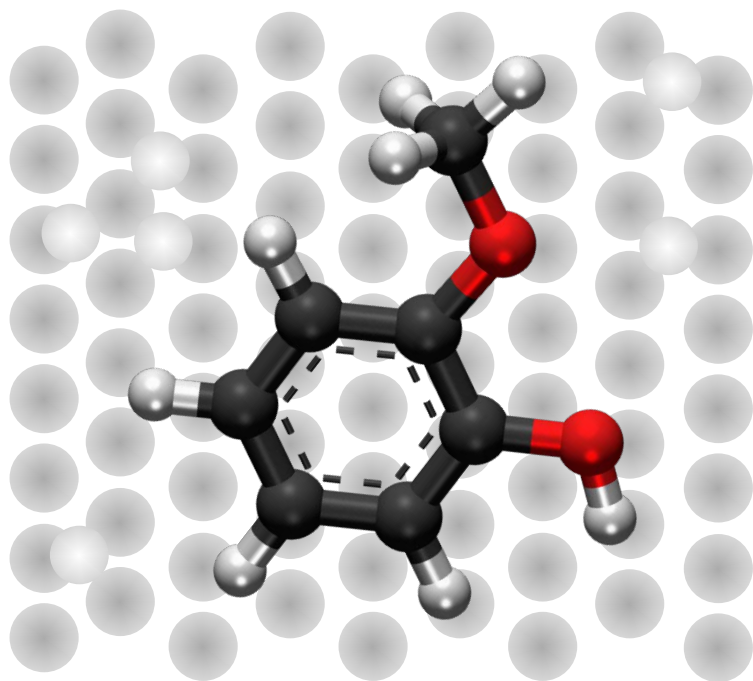
**Table 1** HDO catalyzed by non-noble transition metals (*T* is temperature; *P* is pressure; *t* is time; WHSV is weight hourly space velocity)

Catalyst	Support	Reactor configuration	Operating conditions				Lignin-derived compound	Major products	Ref.
			<i>T</i> (K)	<i>P</i> (bar)	<i>t</i> (h)	WHSV (h <sup>-1</sup> )			
Ni	SiO <sub>2</sub>	Batch	593	170	1	—	GUA	CYHA, CYHAONE	61
Ni	SiO <sub>2</sub>	Batch	593	170	—	—	GUA	CYHA, CYHAONE	132
Ni	SiO <sub>2</sub>	Fixed bed	423	1	0–4	—	Ph	CYHAONE, CYHAOL, Ben	130
Ni	SiO <sub>2</sub>	Fixed bed	423	1	0–4	—	CYHAONE	CYHAOL, Ph, Ben	130
Ni	SiO <sub>2</sub>	Fixed bed	573	50	—	2	ANI	Ph, Ben	117
Ni	γ-Al <sub>2</sub> O <sub>3</sub>	Fixed bed	573	50	—	2	ANI	Ph, Ben	117
Ni	SBA-15	Flow reactor	563–583	3	—	20.4 and 81.6	ANI	Ben	135
	Al-SBA-15								
	γ-Al <sub>2</sub> O <sub>3</sub>								
	Microporous carbon								
	TiO <sub>2</sub>								
	CeO <sub>2</sub>								
Ni	SiO <sub>2</sub> -ZrO <sub>2</sub>	Batch	573–613	50	5	—	GUA	CYHA, MCYHA, PCYHA	133
Ni	ZrO <sub>2</sub> -SiO <sub>2</sub>	Batch	523–613	50	—	—	Ph, GUA	CYHA	158

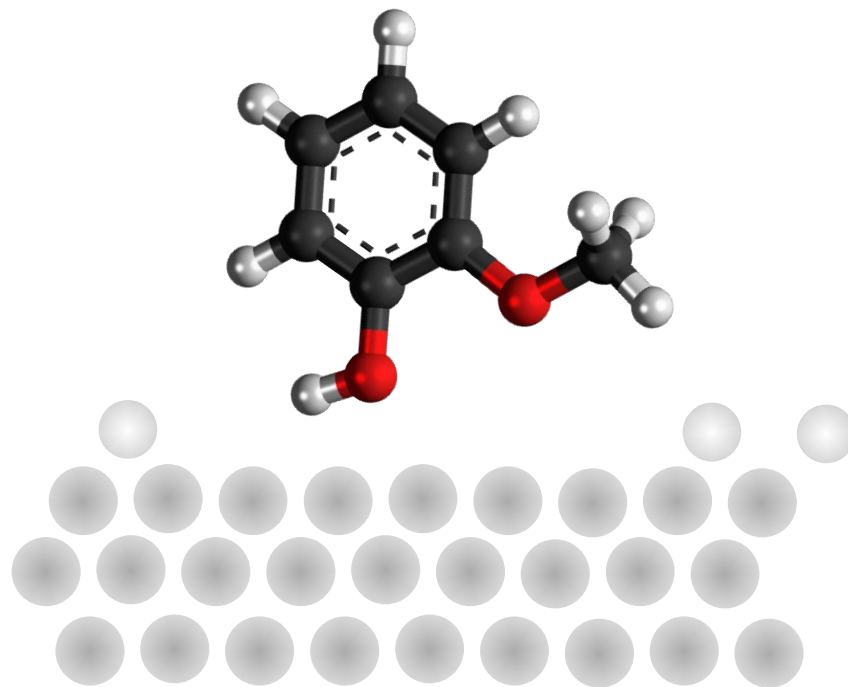
Saidi, M., et al. Energy & Environmental Science 2014:7,103-129.



# ELECTROCHEMICAL DEOXYGENATION - HYPOTHESIS



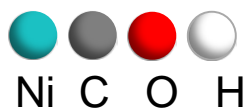
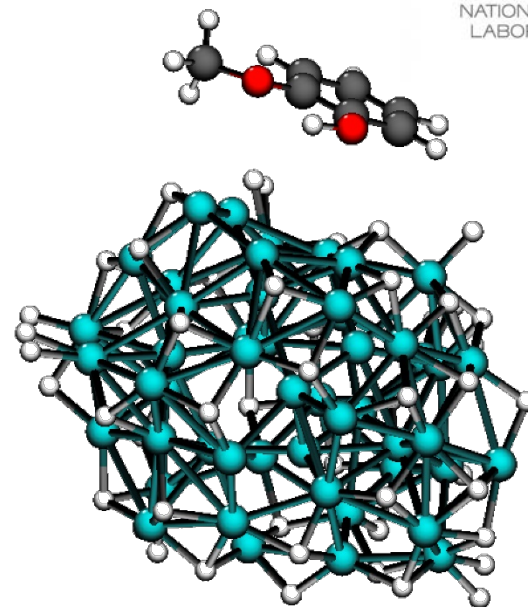
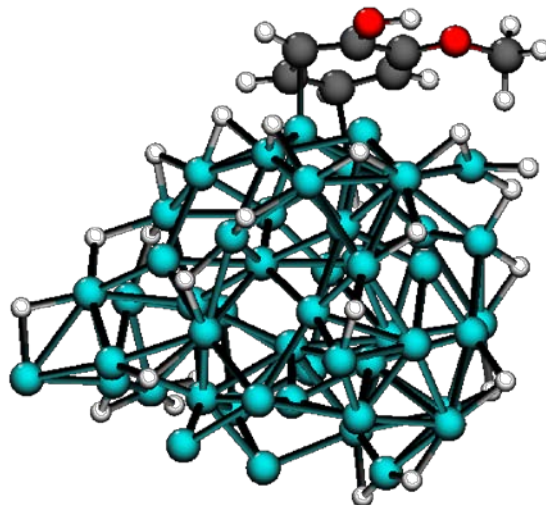
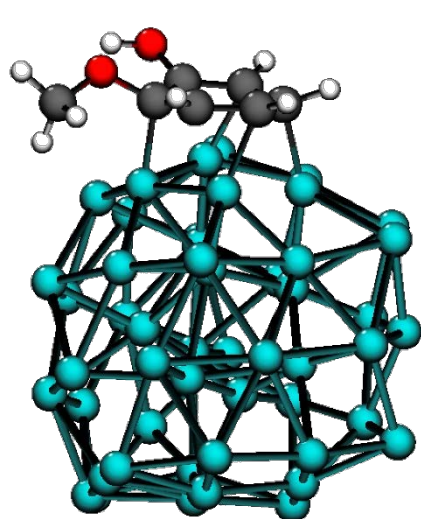
PLANAR adsorption  
Ni<111>



VERTICAL adsorption  
Ni<111>



# HYDROGEN LOADING - THERMAL

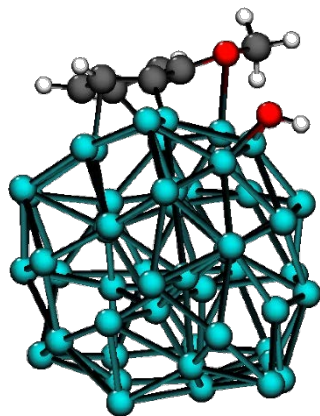


Guaiacol/cluster interactions  
decrease by ~30%  
(2-3 Å from cluster)

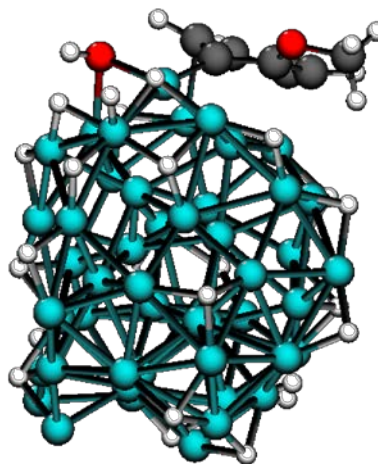
Guaiacol does not bind on  
full H-coverage cluster (~4-5  
Å from metal cluster)



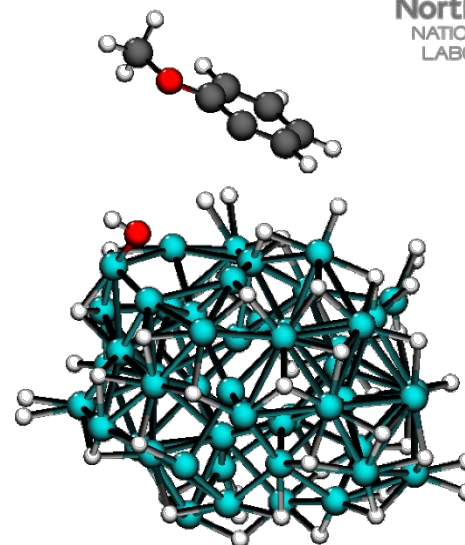
# C-O BOND Dissociation as a Function of H coverage and charge



H Coverage: 0ML



~0.5ML



~1ML

H Coverage	BDE (no charge) (in Kcal/mol)	BDE (charged) (Kcal/mol)
0	-2	0
0.5	24	0
1.0	32	34



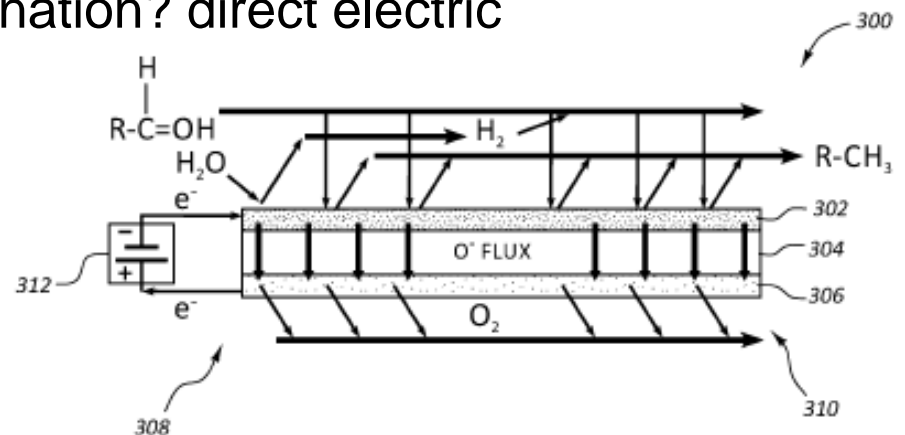
## Consequences of H coverage and Charge on C-O dissociation

- The orientation of organic with respect to the surface changes from planar to angled (almost vertical). Surface/organic contact is needed for effective C-O dissociation
- The Bond Dissociation Energy (BDE) becomes endothermic as the coverage increases
- Charged surface helps dissociation by stabilizing the organic, as long as there is contact
  - At high coverage, the benefit of charged surface becomes irrelevant because the organic/surface orientation/contact are unfavorable
  - H is also stabilized on the surface.

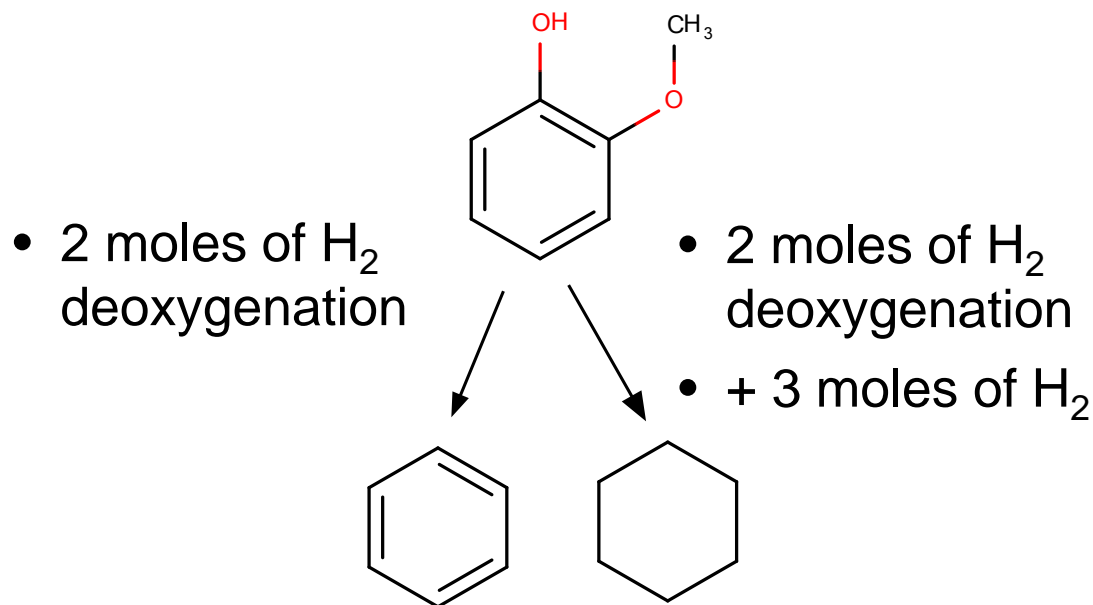


# ELECTROCHEMICAL DEOXYGENATION PROCESS UNDERSTANDING

- In-situ generation of  $H_2$  by electrolysis of bio-oil water
- Role of **electricity**:
  - Stabilize intermediates
  - Alter the adsorption, reduce hydrogen (energy) consumption
  - Increase local hydrogen loading
- To be investigated: ring hydrogenation? direct electric decarboxylation?



# IMPLICATIONS FOR LCA

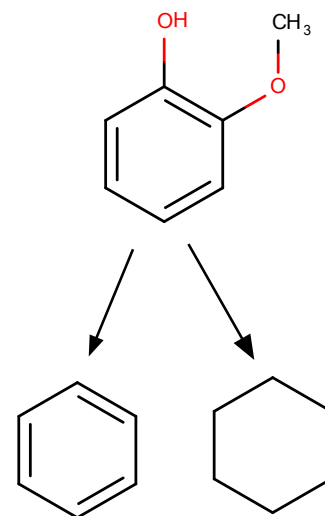


- Less H<sub>2</sub> consumption, less energy
- More versatile (valuable) deoxygenation products (aim for phenols or BTEX)

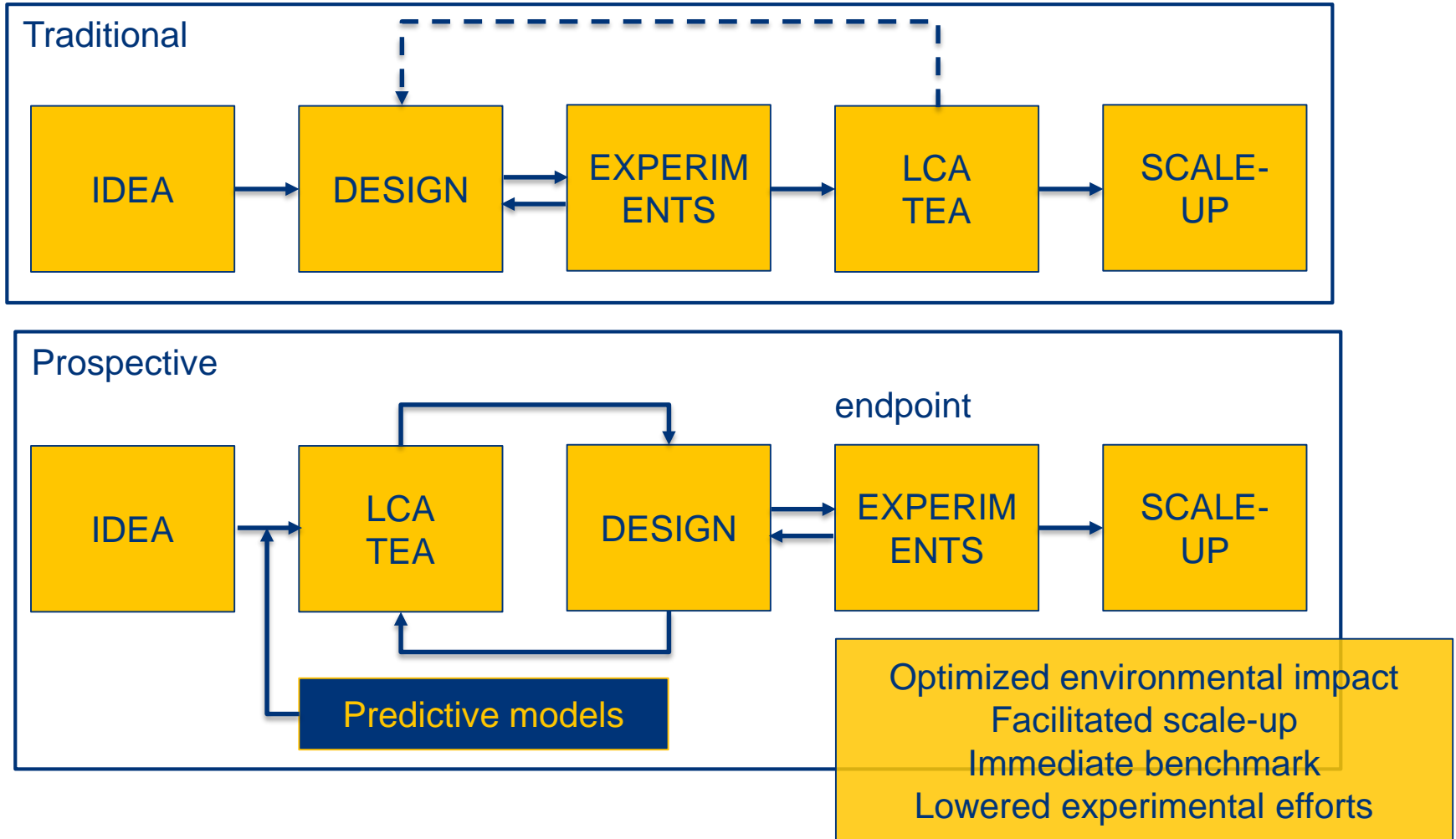


# Implications for Prospective LCA

- Can use DfT in 2 ways:
- A priori: simulations are tested to drive the desired reactions (optimizing valuable compounds; reducing H and energy input) prior to experimentation
- A posteriori: simulate to understand the possible reaction mechanisms from products generated from experiments



# (Prospective) Life Cycle Design



## RELEVANCE

Engineering = decision making

$$\max S = \sum_i P_i x_i - (C_{fix} + C_{var} \sum_i x_i + \sum_i c_{m,i} x_i)$$

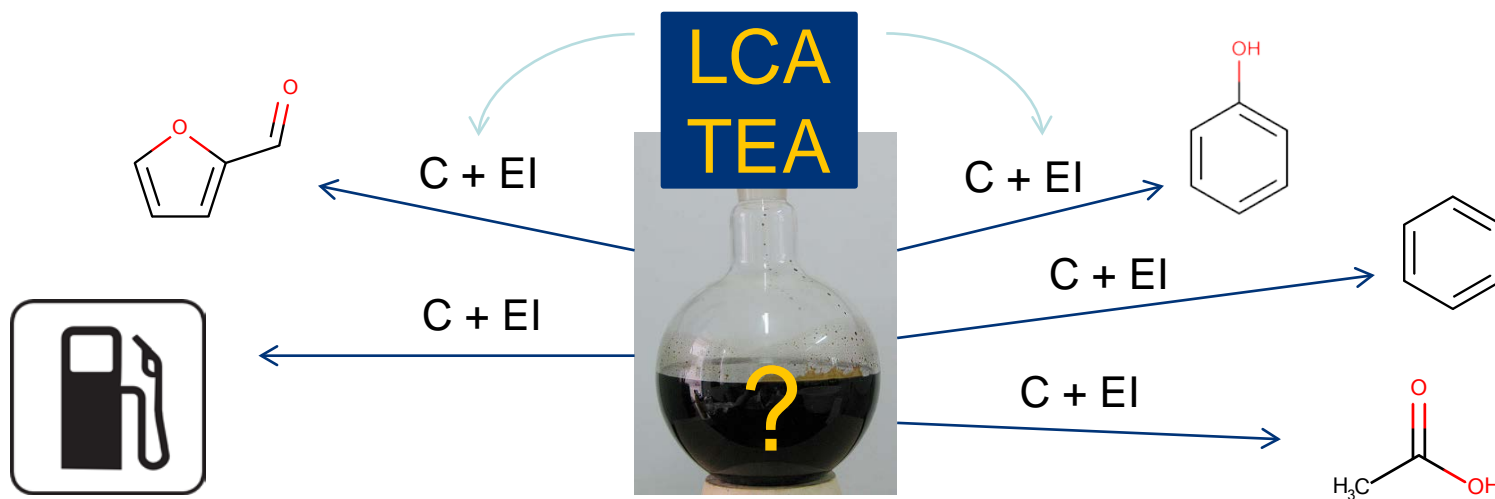
s. t.

$$(EI_{indirect} + EI_{direct} \sum_i x_i) - \sum_i EI_{trad,i} x_i < 0$$

$$\sum_i carbon_i \cdot x_i - carbon_{BO} \cdot X_{BO} \leq 0$$

$$descendants \sum_{j=n}^{n+m} x_j \leq ancestor \text{ compound } x_{BO}$$

$$x_i \geq 0$$



EI = Environmental Impact  
C = Cost



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## ACKNOWLEDGEMENT

Bio-oil upgrading work is supported by the **DOE-EERE** Award Number DE-EE0006288 under the **Carbon, Hydrogen and Separation Efficiencies in Bio-Oil Conversion Pathways (CHASE Bio-Oil Pathways)**



S. Elangovan, J. Hartvigsen, D. Larsen, J. Ellwell,  
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Technology Holding Inc. – M. Karanjikar

# Acknowledgements

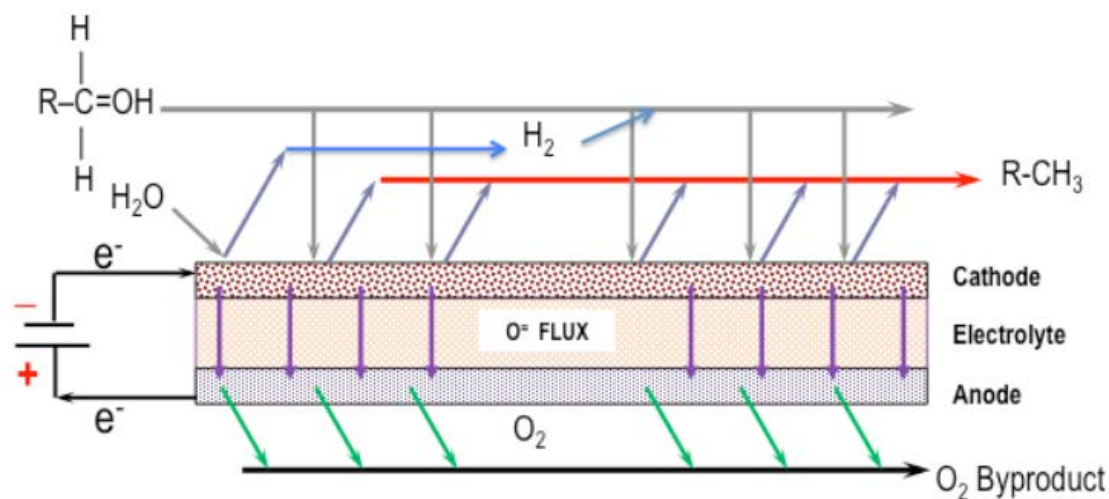
- P. Billen (U. Antwerp), Y. Sorunmu, B. Riaz (Drexel), AA Boateng, C.A. Mullen, Y. Elkasabi (USDA-ARS),
- Research supported by the DOE-EERE Award Number DE-EE0006288; USDA-NIFA: 2012-10008-20271; and NSF CMMI-1550723

# General EDOx Reaction Mechanism

Cathode :

Steam electrolysis:  $2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$

Deox rxn:  $\text{R-CH}_2\text{OH} + \text{H}_2 \rightarrow \text{R-CH}_3 + \text{H}_2\text{O}$



Anode:

Oxygen exits from the anode side



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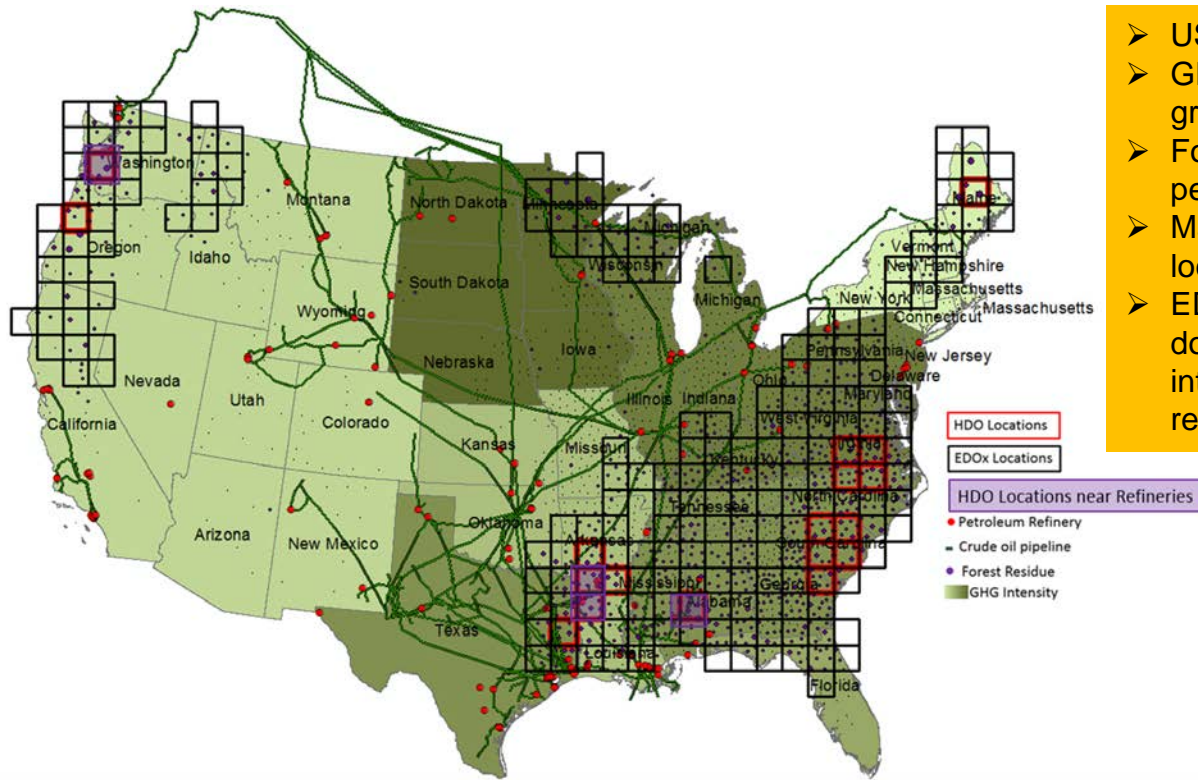
# Challenges in Modeling Early Stage Transport Fuel Technology

Sabrina Spatari, PhD, P.Eng



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# How many EDOx and HDO units can be sited?



- US map showing EDOx and HDO locations
- GHG intensity (CO<sub>2</sub> eq.) varies by electricity grid
- Forest residue availability is in billion dry tons per year (bdtpy)
- Map shows more possibilities of EDOx locations than HDO
- EDOx locations near petroleum refineries (red dot) show opportunity for improving intermediate product transport/logistics in relation to final upgrading

