Flexibility in Biofuel Manufacturing

Dan Gaspar

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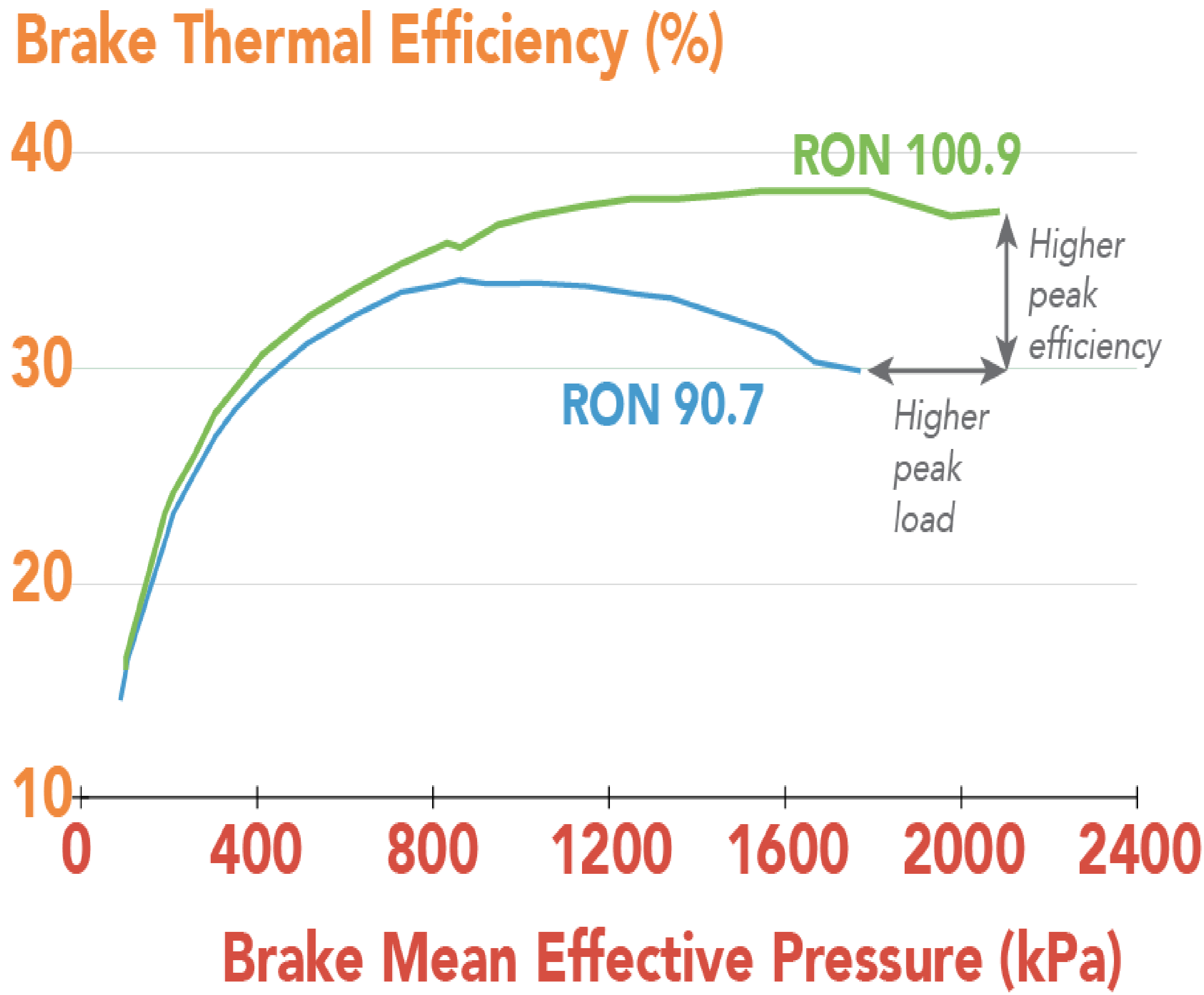
Governing Co-Optima hypotheses:

There are engine architectures and strategies that provide higher thermodynamic efficiencies than available from modern internal combustion engines; new fuels are required to maximize efficiency and operability across a wide speed/load range

If we identify the **critical fuel properties** and target values that maximize efficiency and emissions performance for a given engine architecture, then fuels that have properties with those values (**regardless of chemical composition**) will provide comparable performance

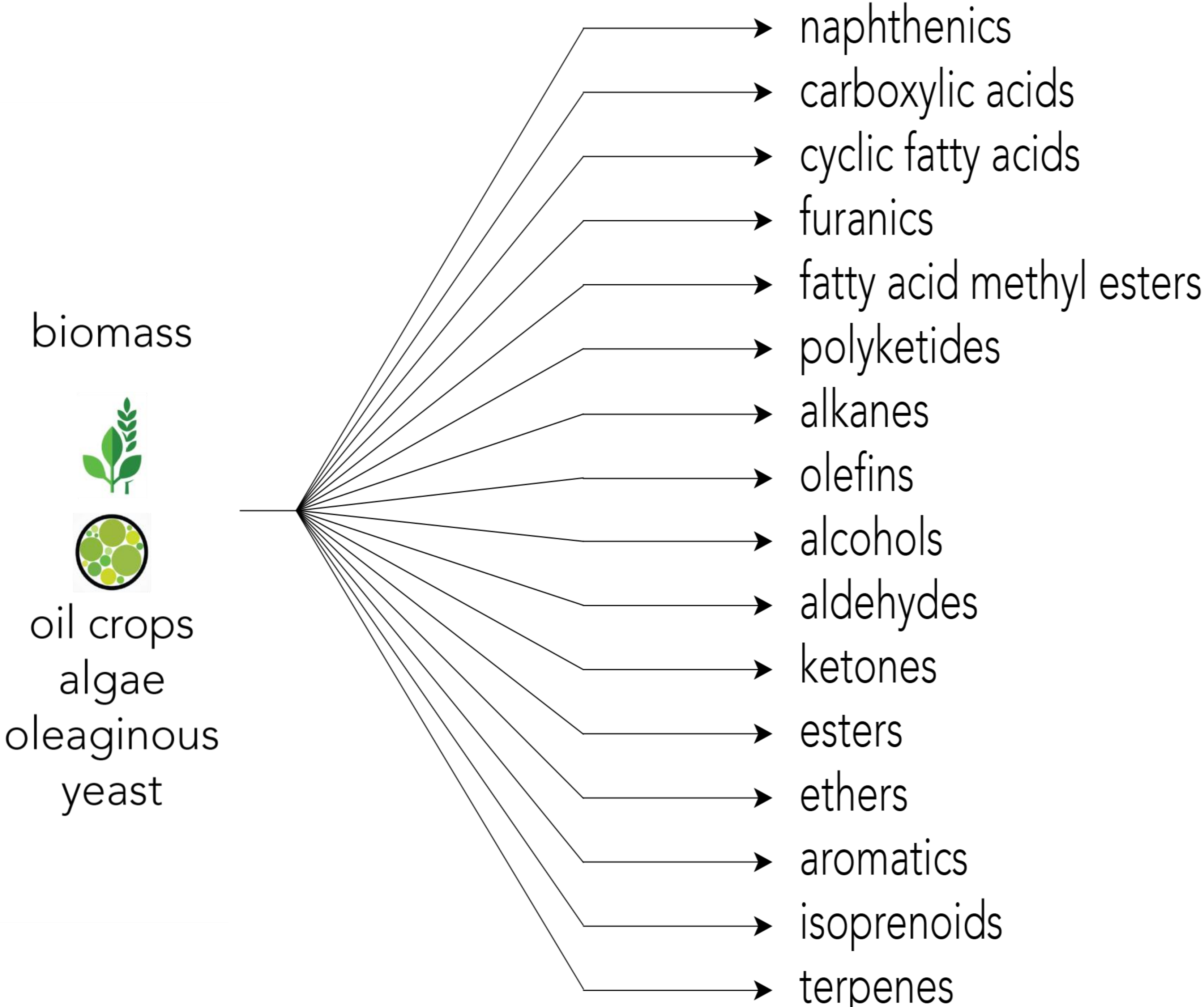
Current fuels **constrain** engine design



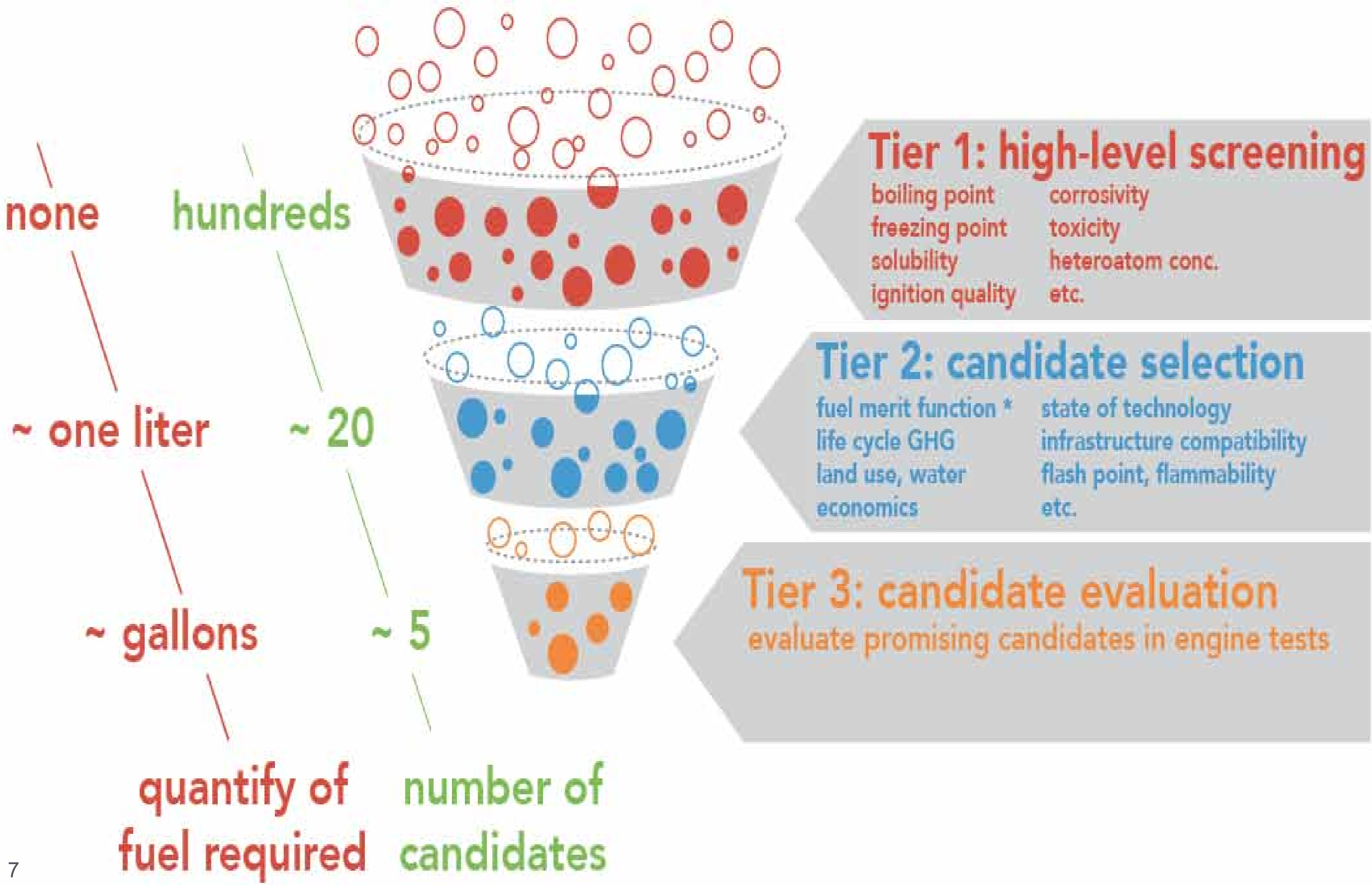
Engine: Ford Ecoboost 1.6L 4-cylinder, turbocharged, direct-injection, 10.1 CR source: C.S. Sluder, ORNL

RON viscosity volatility MON cloud point
bulk modulus of compressibility Wobbe index heating value
sensitivity heat of vaporization
soot precursor formation PMI flammability limits smoke point
cetane number T50
heat of combustion flame stretch ignition limits
C/H ratio strain sensitivity
density specific heat ratio
naphthene level Markstein length
T10 surface tension flash point T90
exergy destruction olefin level
energy density sulfur level
laminar burning velocity
diffusivity drivability index flame speed
aromatics level oxygenate level

What fuels can we make?
What fuels *should* we make?


biomass
oil crops
algae
oleaginous
yeast
naphthenics
carboxylic acids
cyclic fatty acids
furanics
fatty acid methyl esters
polyketides
alkanes
olefins
alcohols
aldehydes
ketones
esters
ethers
aromatics
isoprenoids
terpenes

Fuel selection criteria ("decision tree")



Thrust I (spark ignition) Tier 1 decision tree results for *functional groups*

- Hydrocarbons
  - Normal paraffins
  - Iso-paraffins
  - Cycloparaffins
  - Aromatics
  - Multi-ring aromatics
  - Olefins
- Carbonyls
  - Ketones
  - Aldehydes
- Esters
  - Simple/volatile fatty acid esters
  - Fatty esters
- Carboxylic Acids
- Alcohols
- Ethers
  - Cyclic/furanics
  - Linear

YES

- Normal paraffins
- Iso-paraffins
- Cycloparaffins
- Olefins
- Alcohols

YES FOR SOME

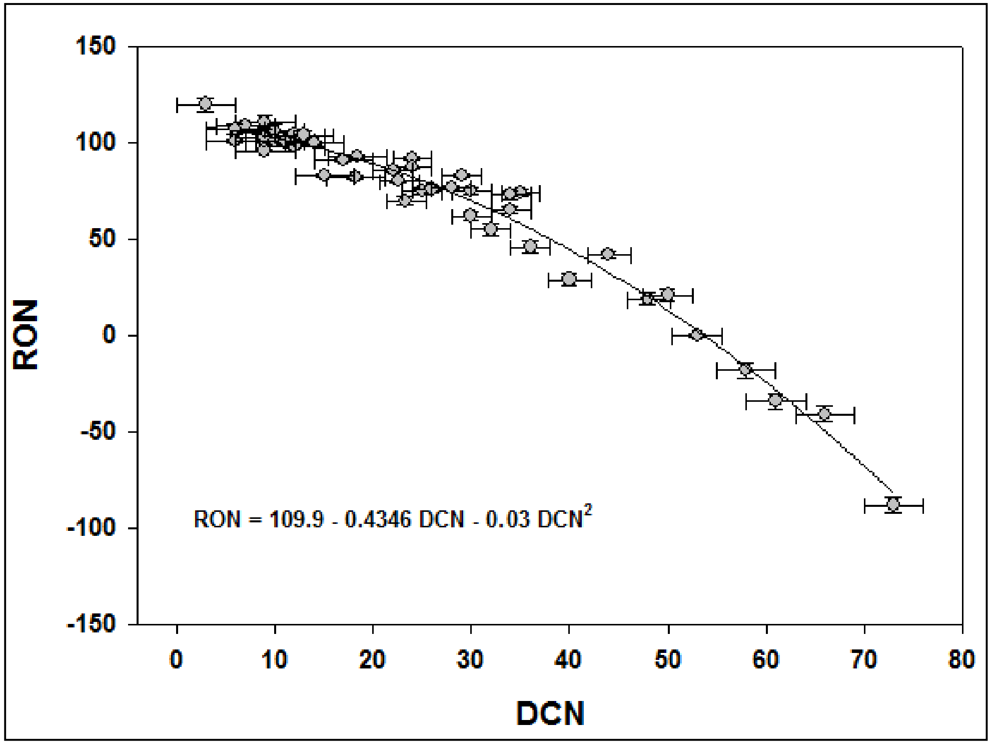
- Aromatics
- Ketones
- Simple/volatile fatty acid esters
- Cyclic ethers/furanics
- Linear ethers

NO

- Multi-ring aromatics
- Aldehydes
- Fatty esters
- Carboxylic acids

Measuring or Estimating RON

- RON was measured for many pure components and blends by ASTM D2699
- If only small quantity available, DCN was measured and RON was predicted from RON-DCN correlation
- For a few compounds, DCN was predicted from a group contribution method, then RON predicted from RON-DCN



Fuel property database

Database of critical fuel properties of bio-derived and petroleum blendstocks

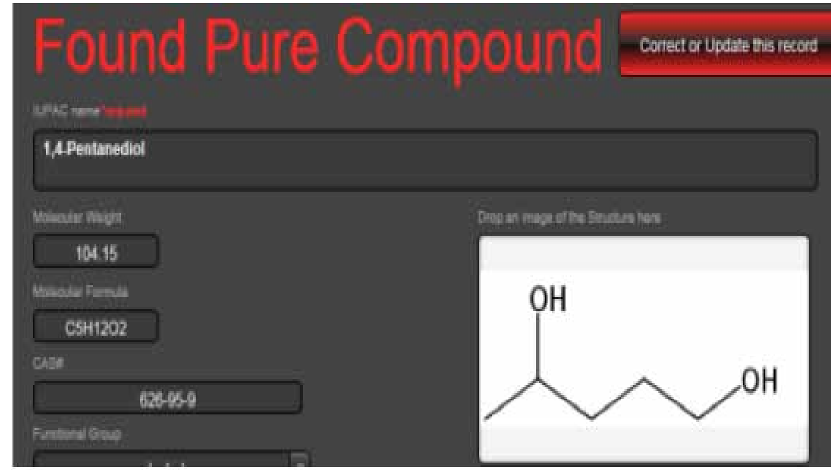
400+ molecules, 12 mixtures (at present)

25 database fields for fuel properties

Will add capability for fully blended fuels

Data from experiment and literature or calculated/estimated (where needed)

Shared resource for team and public



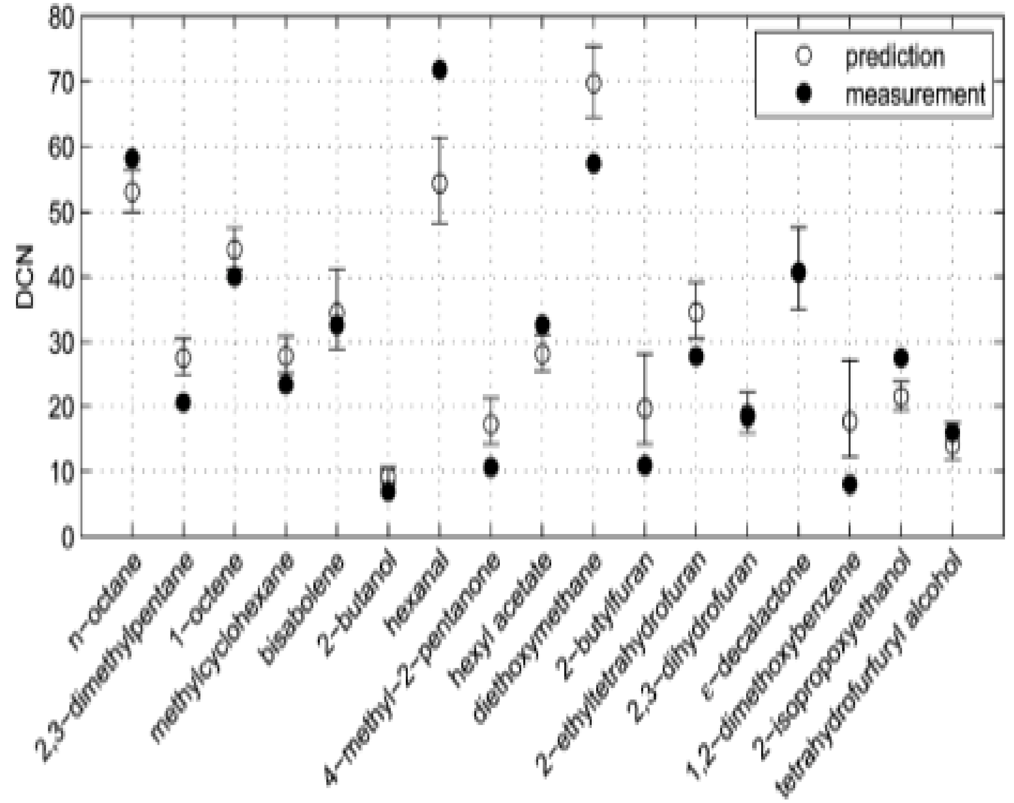
Fioroni et al., NREL

Biofuel structure guidance tools

Predictive tools of structure-performance relationships

Provide guidance to fuel discovery efforts

Varying degree of fidelity – machine learning, QSAR, quantum chemistry



From Dahmen and Marquardt, *Energy Fuels,* 2015, 29 (9), pp 5781–5801

DOI: 10.1021/acs.energyfuels.5b01032

Identification of Thrust I candidates

Tier I criteria

Melting point/cloud point below -10?C

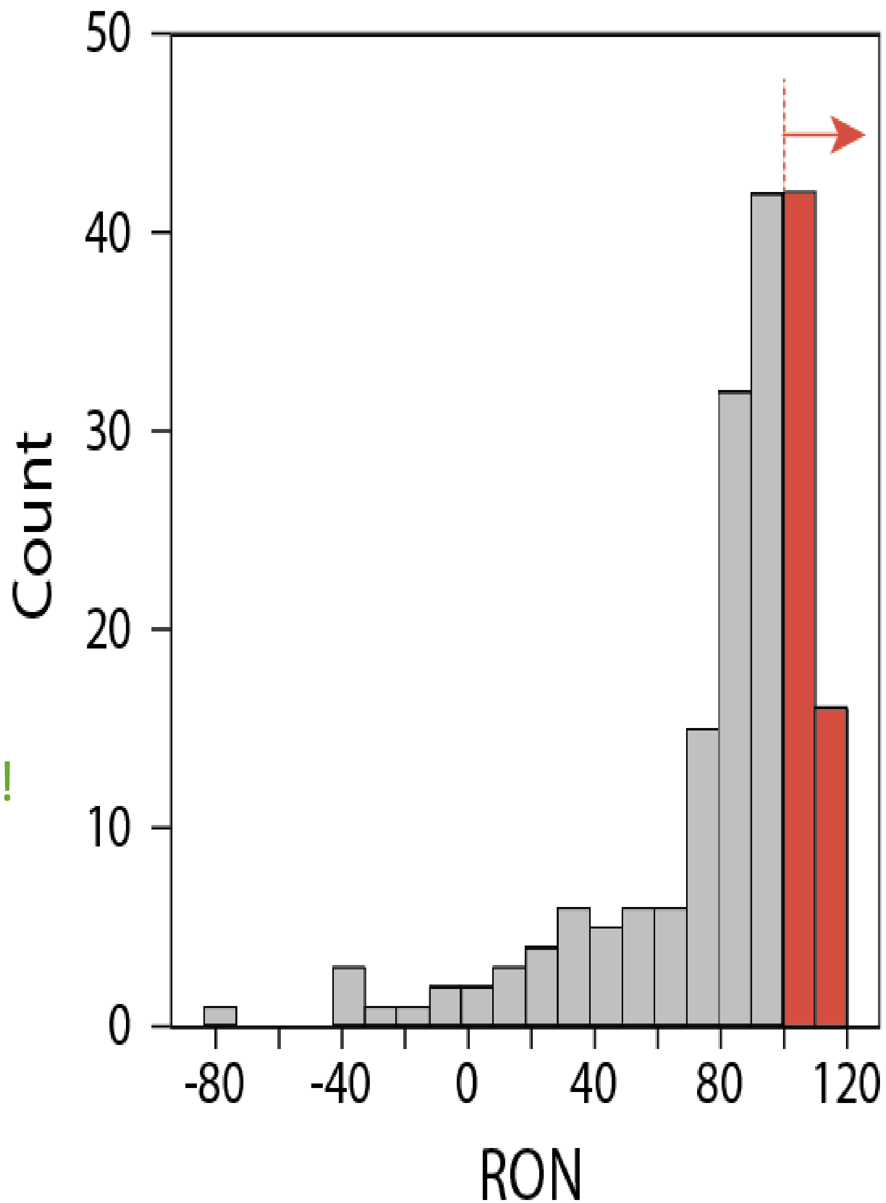
Boiling point between 20?C and 165?C

Measured or estimated RON ≥ 98

Meet toxicity, corrosion, solubility, and biodegradation requirements

40+ promising bio-blendstocks from many functional group classes

Not final – this is an iterative process!



Engine performance merit function

Provides systematic ranking of bio-blendstock candidates on engine efficiency when multiple fuel properties are varying simultaneously

Allows fuel economy gains to be estimated based on fuel properties

$$Merit = \frac{(RON_{mix} - 92)}{1.6} - K\frac{(S_{mix} - 10)}{1.6} + \frac{0.01[ON/kJ/kg](HoV_{mix} - 415[kJ/kg])}{1.6}$$
$$+ \frac{(HoV_{mix} - 415[kJ/kg])}{130} + \frac{(S_{L\,mix} - 46[cm/s])}{3}$$
$$- LFV_{150} - H(PMI - 2.0)[0.67 + 0.5(PMI - 2.0)]$$

RON = research octane number
K = engine-dependent constant
S = sensitivity (RON-MON)
ON = effective octane number
HoV = heat of vaporization
S_L = flame speed
LFV = liquid fuel volume at 150° C
H = Heaviside function
PMI = particle mass index

Cost and environmental impact analyses

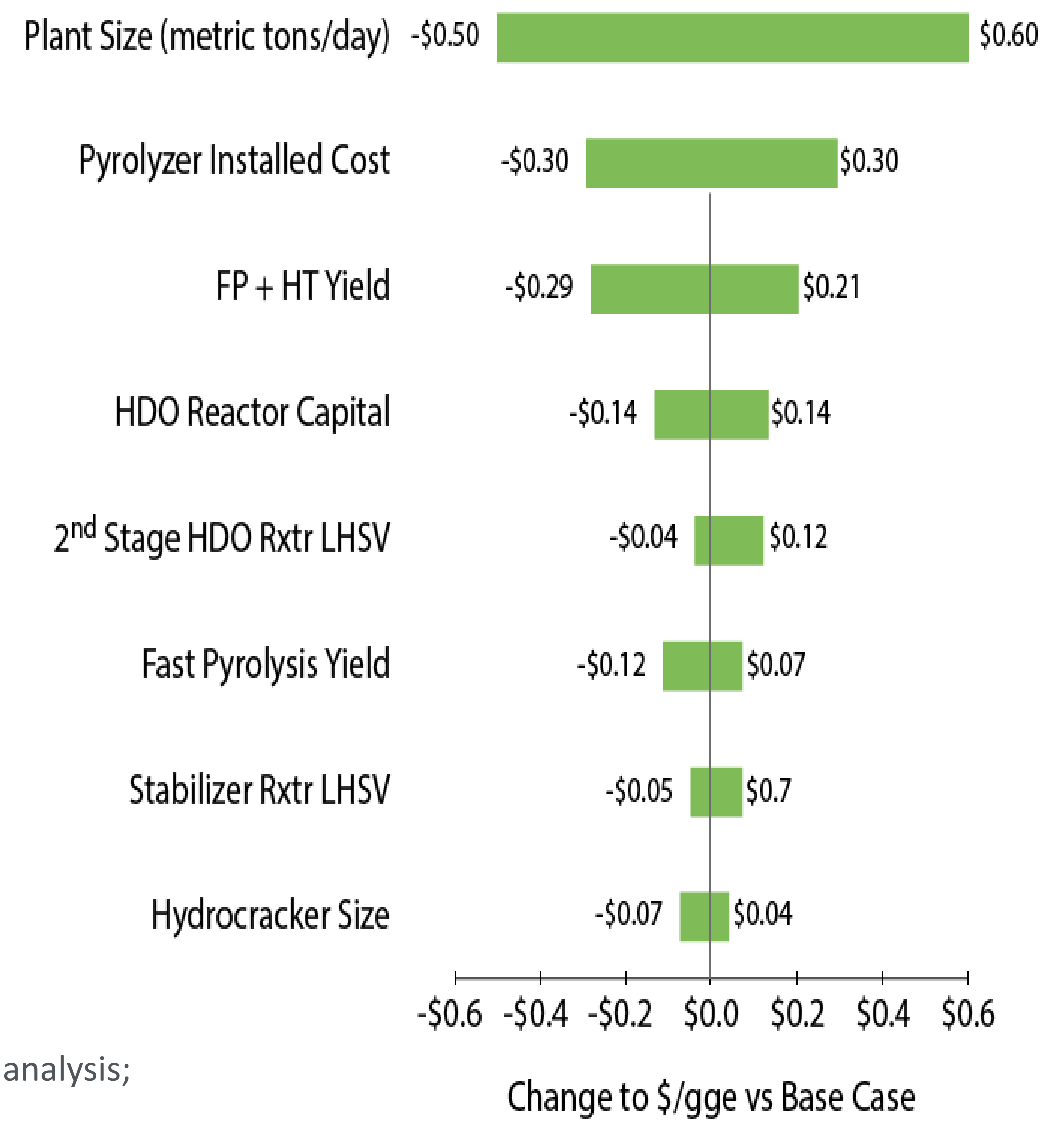
High-level LCA, TEA,*
feedstock availability analyses

Identify cost/environmental/scale attributes

Fifteen key metrics identified

GHG, water, economics, TRL

Evaluation of 20 Thrust I blendstocks underway



* LCA = Life cycle analysis; TEA = techno-economic analysis; TRL = technology readiness level

Next Steps

FY16

- Finish Tier 2 measurements on 40+ high RON bio-blendstocks
- Complete initial blending experiments (bRON, bMON) on select high RON bio-blendstocks

FY17

- Complete flame speed measurements for high-priority Thrust 1 candidates
- Extend fuel property database
- Perform retrosynthetic analysis on high RON bio-blendstocks
- Extend blend model development to high-priority Thrust 1 bio-blendstocks
- Initiate analysis of diesel-like Thrust 2 bio-blendstocks

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Co-Optima Technical Team Leads:

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Other Co-Optima Leadership Team Members:

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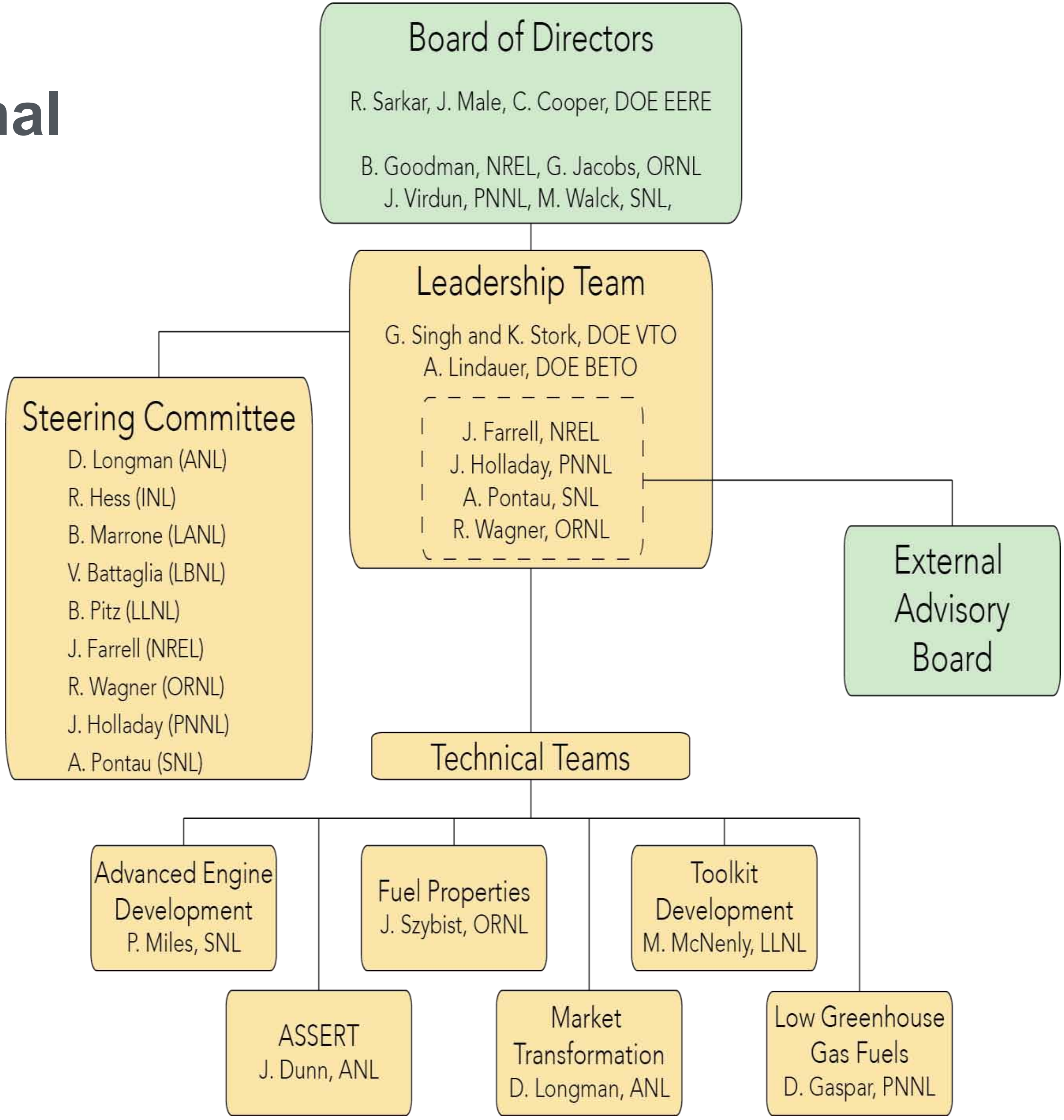
Thank You

Back-up Slides

Co-Optima organizational structure



Six integrated teams

Low Greenhouse Gas Fuels

LGGF

Identify promising bio-derived blendstocks, develop selection criteria for fuel molecules, and identify viable production pathways,

Advanced Engine Development

AED

Quantify interactions between fuel properties and engine design and operating strategies – enabling optimal design of efficient, emission-compliant engines

Fuel Properties

Fuels

Identify critical properties and allowable ranges, systematically catalogue properties, and predict fuel blending behavior

Modeling and Simulation Toolkit

TK

Extend the range, confidence and applicability of engine experiments by leveraging high-fidelity simulation capabilities

Analysis of Sustainability, Scale, Economics, Risk, and Trade

ASSERT

Analyze energy, economic, and environmental benefits at US economy-level and examine routes to feedstock production at scale through existing biomass markets

Market Transformation

MT

Identify and mitigate challenges of moving new fuels and engines to markets and engage with full range of stakeholders

Co-Optima Charter

Provide stakeholders with the comprehensive, objective, science-based, and actionable data on engine systems and transportation fuels required to identify the most promising options for large-scale commercial introduction

Priority will be given to fuel/engine combinations that maximize the role of the market and have fewer barriers to wide-scale deployment

Our role is not to pick winners and losers (we do not produce fuels or make engines).

Actionable data on engine systems and transportation fuels include:

- *Robust engine data (efficiency and emissions) based on experiment and simulation.*
- *Identification of critical fuel properties and relative importance for each engine operating strategy.*
- *Identification of promising low-GHG blendstocks and pathways for their production.*
- *Characterization of impact of blendstock impurities that will arise in production.*
- *Quantification of fuel blending behavior (oxygenates and hydrocarbons).*
- *Development and validation of fuel property-based hypothesis*
- *Analysis of sustainability, economics, and market barriers for promising low-GHG blendstocks*