SAND2012-0501P

Tailoring Next-Generation Biofuels and their Combustion in Next-Generation Engines

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BSAP Review 2012,
Sandia National Laboratory

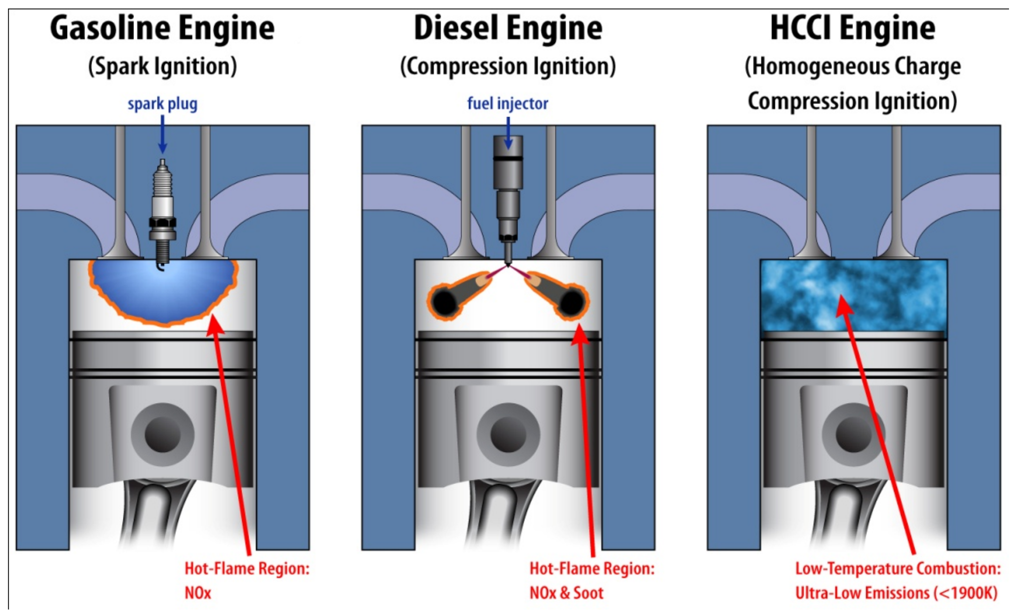
Fuel Chemistry and Engine Combustion Efficiency are Interdependent

Advanced clean efficient (>30% improvement) engines (e.g., HCCI) rely on compression ignition – chemistry – to time combustion.

Increased use of biofuels will change fuel chemistry dramatically.

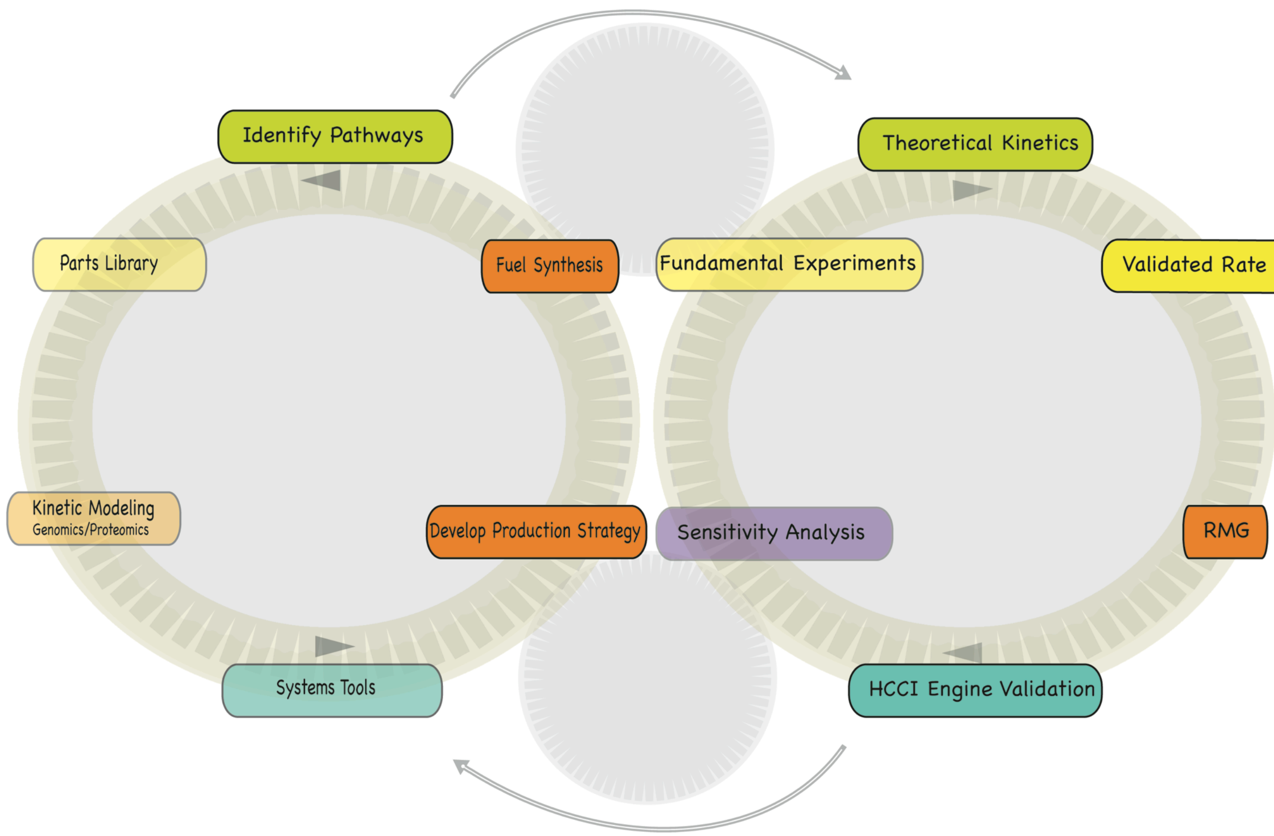
Previous (even minor) fuel changes have been disruptive.

New fuel chemistry could *enable* advanced engines.



However, biofuel development is typically isolated from combustion performance investigations.

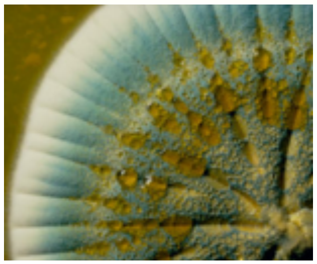
Overarching goal: *Robust framework* for biofuel/engine Co-development



Adaptable framework – beyond any specific set of production or utilization platforms
Represents a new way to engineer biofuels

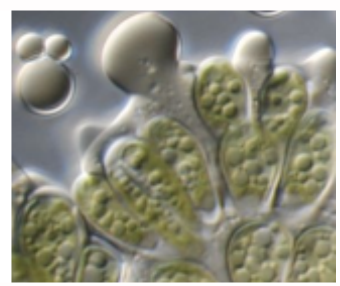
Diverse Chemistry in Nature

Pathways rewiring, integration and lab. evaluation



Anti-bacterial/fungal, antineoplastic, pharmaceuticals

Biomaterials



Energetic molecules

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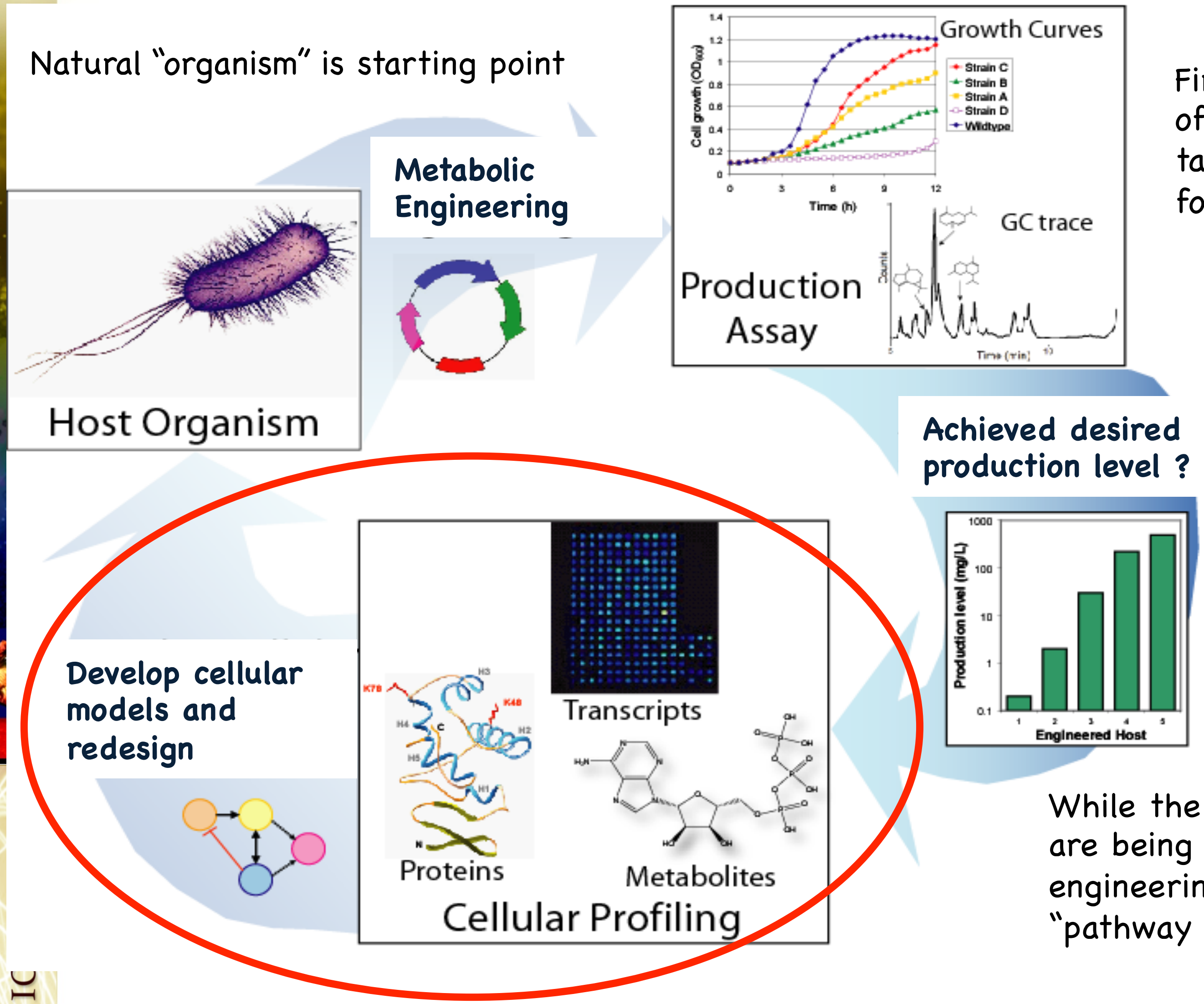
Optimization loop for biofuel production should mesh with combustion investigations

Natural "organism" is starting point



First "mesh point" is analysis of VOC output, identification of targets
for combustion studies

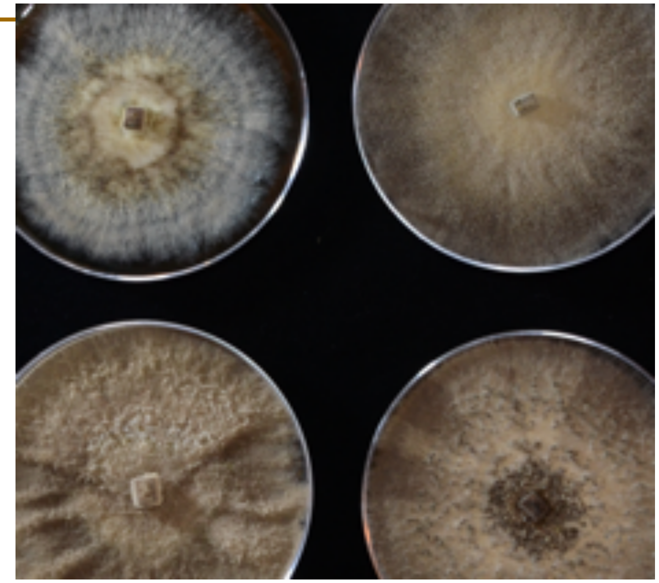
Second mesh point: Combustion performance is part of feedback for desired production level

While the combustion modeling tools are being developed, the biochemical engineering toolkit is assembled – "pathway prospecting"

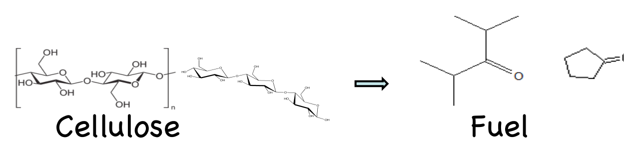
Fungal Endophytes are Tunable Platforms

direct cellulosic biomass conversion to hydrocarbon

- Endophytes have substantial advantages for biofuel production.
  - Live within a host for part of their life without causing disease.
  - Minimal genomes – much like recent attempts to make tailored strains.
- Endosymbionts can directly convert cellulose into hydrocarbons.
- We have focused our efforts on endophytic fungi that have been shown to produce a range of moderate-molecular weight hydrocarbons (volatile organic compounds – VOC).



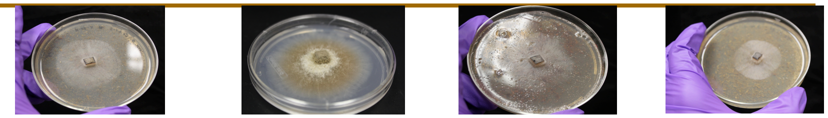
Fungi can directly consume cellulose and other renewable carbon compounds, produce a spectrum of potentially useful volatile organic compounds (VOC)



Ascomycota (sac fungi) – 300 million yrs

Cellulosic Biomass Supports Fungal Growth

- Radial growth is effected by the nature of the feedstock.
- Daldinia seems to care the least.
- Four other isolates have also been profiled and three others are in the pipeline.



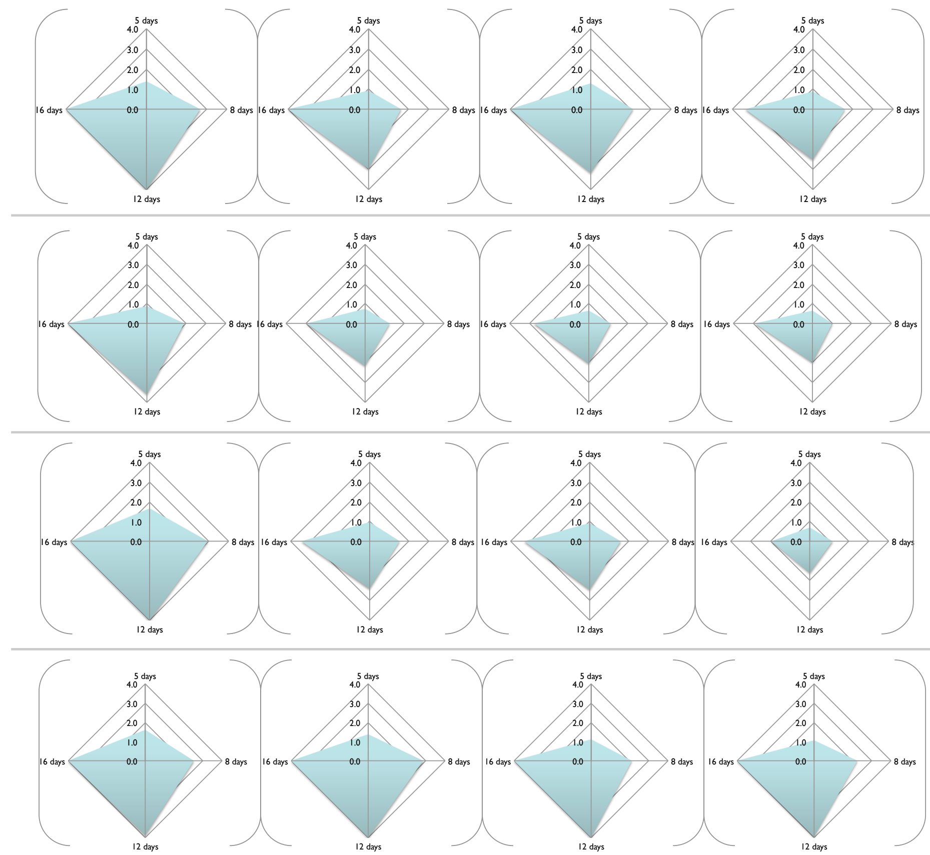
PDA | Corn Stover | Eucalyptus | Switch Grass

CO 27-A

EC 38

C14-A

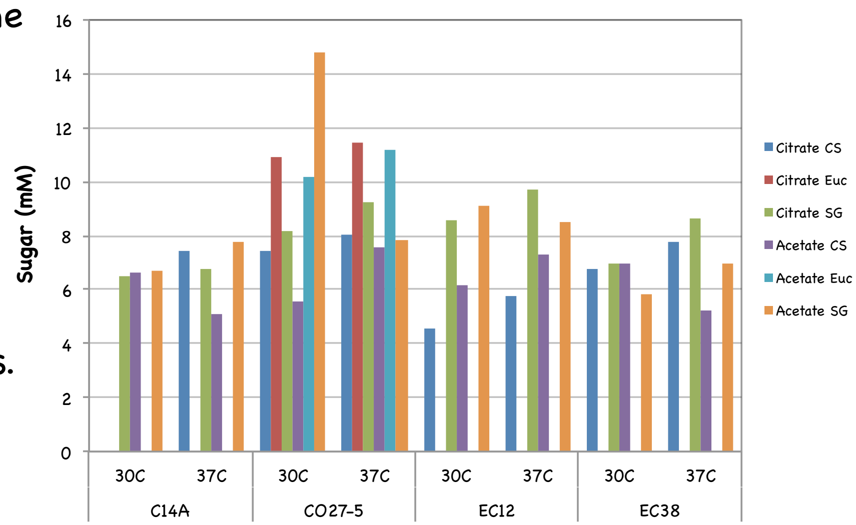
Daldinia



Fungal Secretome Encodes Cellulolytic Activity

biomass degradation potential over wide temperature and pH range

- Endophytes were grown on cellulosic feedstock as the sole carbon source (corn stover, switchgrass, eucalyptus and potato dextrose).
- Secreted proteins were assayed for cellulolytic activity.
- Enzyme activity over a wide pH and temperature range was confirmed using established in vitro assays.
- Follow-up experiments are under way to identify functional classes and secretion pathways.

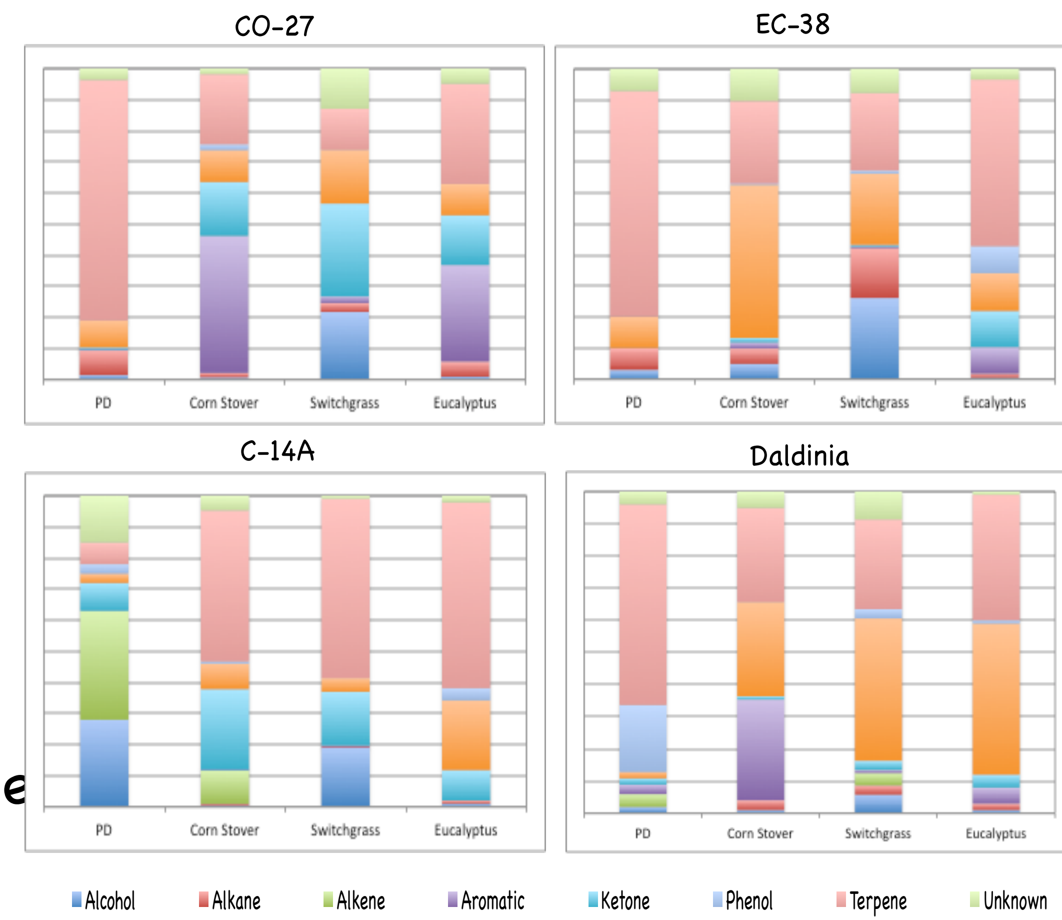


Hydrocarbon Profile is Tunable

- VOC profile changes as a function of feedstock.
- A number of compounds that have fuel properties.
- A few of these have been studied for their ignition chemistry characteristics.
- Biological mechanism responsible for hydrocarbon production required genome sequencing and reconstruction.

- Proteomics will be used to further characterize these pathways.

- Criteria for combustion chemistry study:
  - Prominence in VOC profile
  - Poor understanding of ignition chemistry



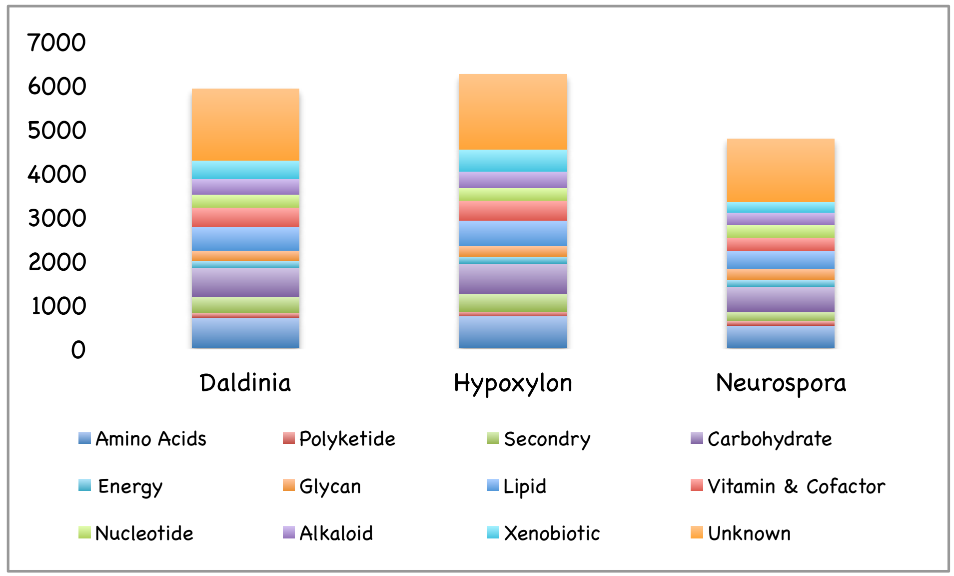
Genome Analysis

cDNA and Genome Sequencing

- Four endophytes genomes sequenced.
  - first reported sequences for such organisms.
- Two have been annotated.
  - two in progress

	CO-27	EC-38	C-14A	Daldiana
Genome Size	40	38	37.1	37.4
Contigs	assembly	assembly	1044	641
Contig Size	assembly	assembly	179	208
Coverage			50x	48x

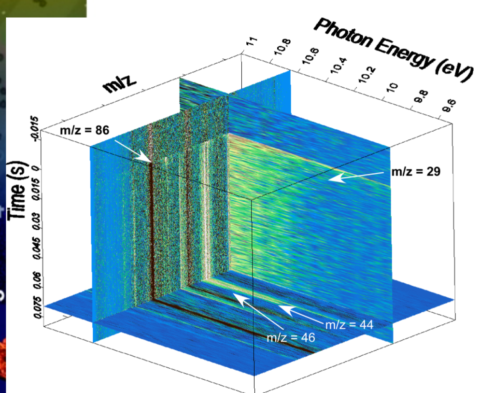
- Transcript analysis using RNA-Seq
  - 99 % match to the genomic data.

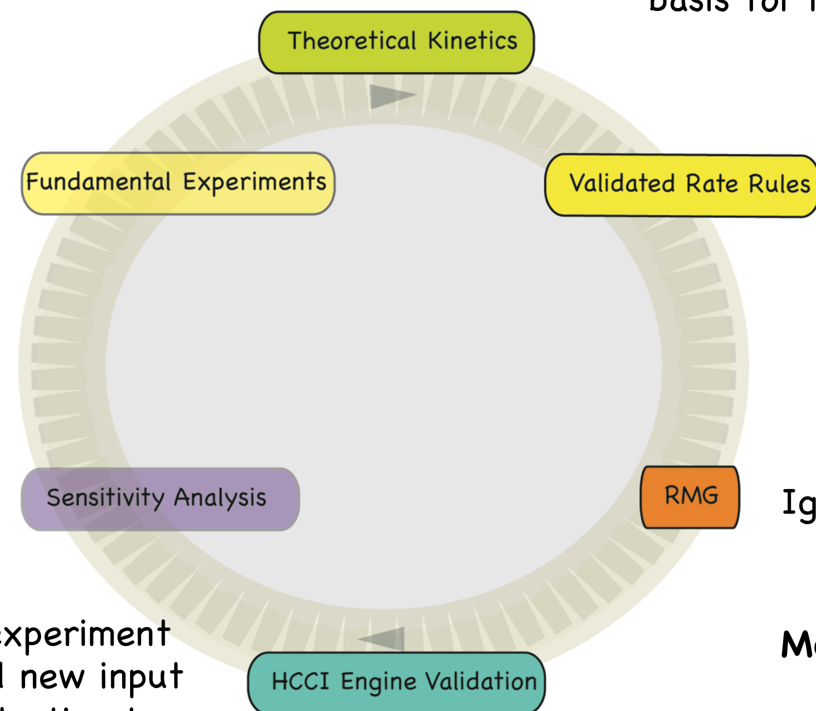


Fundamental chemistry measurements are the first step in the combustion model

Molecular structure affects key elementary autoignition reactions

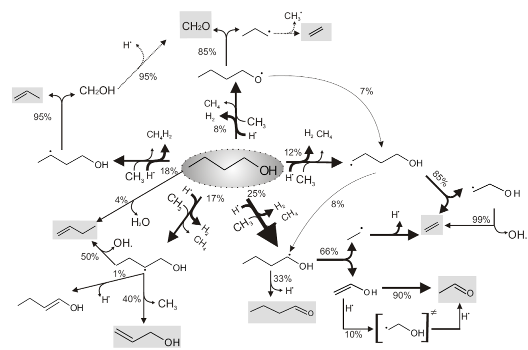
Mesh point – target representatives of classes of molecules in fungal VOC profiles





Integrating the key reactions into an overall ignition model uses the RMG toolkit from Bill Green (MIT)

Structure-dependent rate rules are the basis for model generation



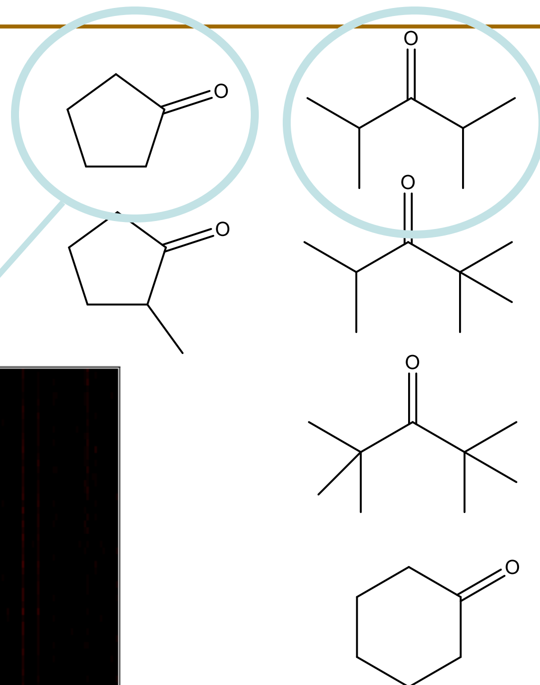
Ignition model is tested in HCCI engine or by bulk ignition measurements

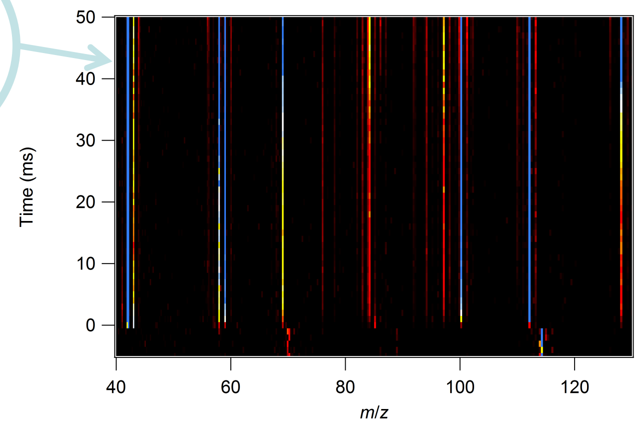
Mesh point -- validated model allows fuel performance feedback to the production side

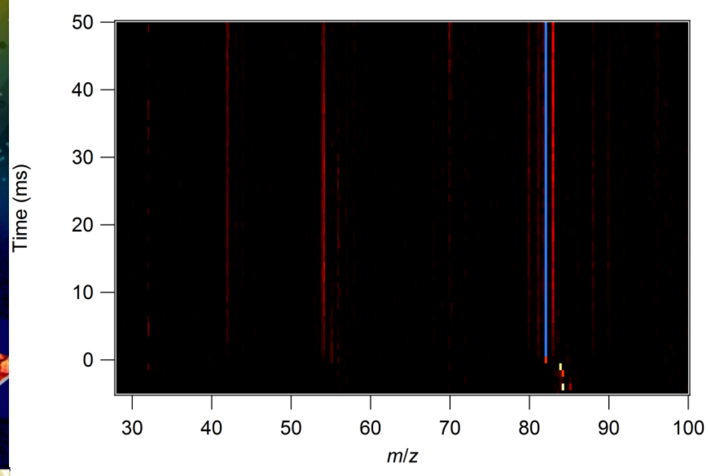
Analysis of model / experiment discrepancies and new input from biofuel production team determine next targets

First targets: ketones and Cyclic ethers
Fundamental Ignition Chemistry Measurement

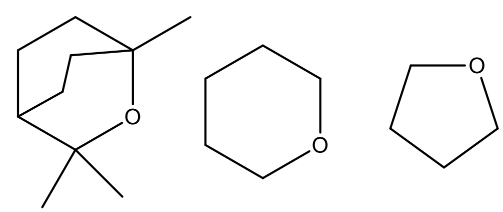
2,4-dimethyl-pentan-3-one (Di-Isopropyl Ketone –DIK) and cyclopentanone







Measurements for cyclic ethers have also been carried out – cineole, oxane, oxolane



Measurements at the Advanced Light Source

probe isomeric products of initial oxidation reactions

Representative ketones chosen to constrain rules for branching near carbonyl site, ring strain

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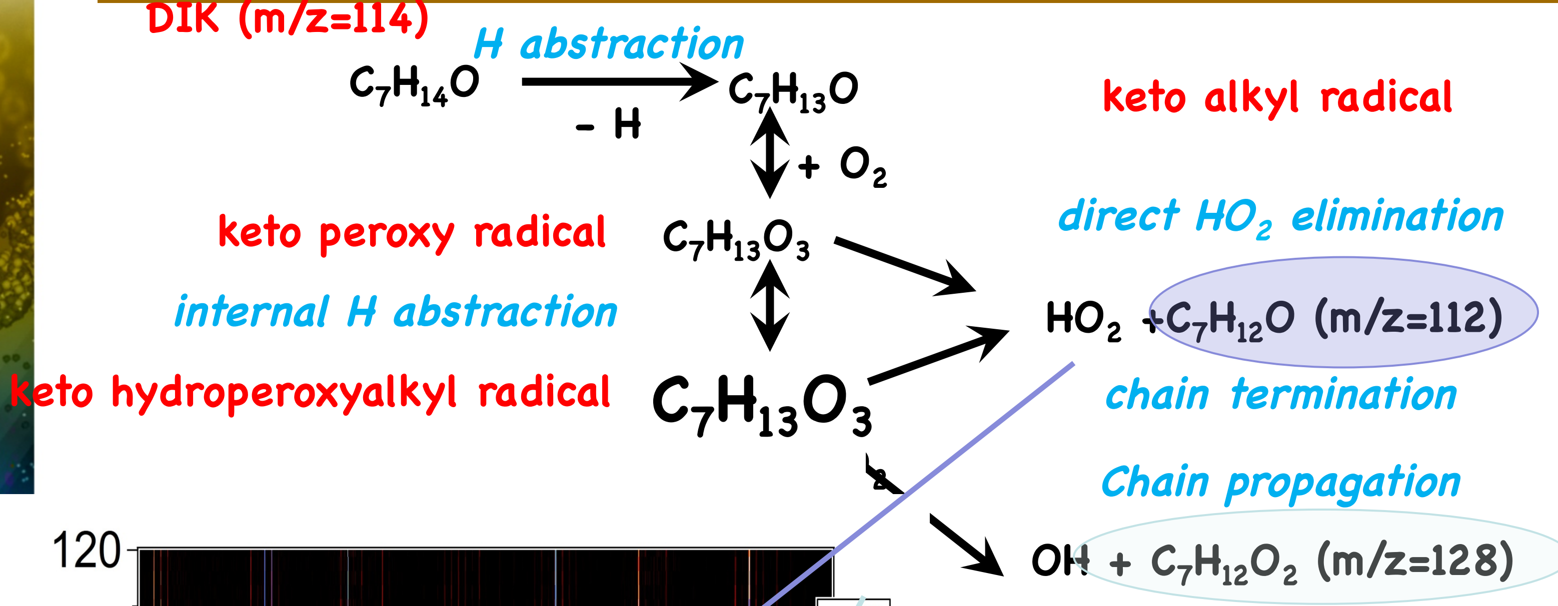
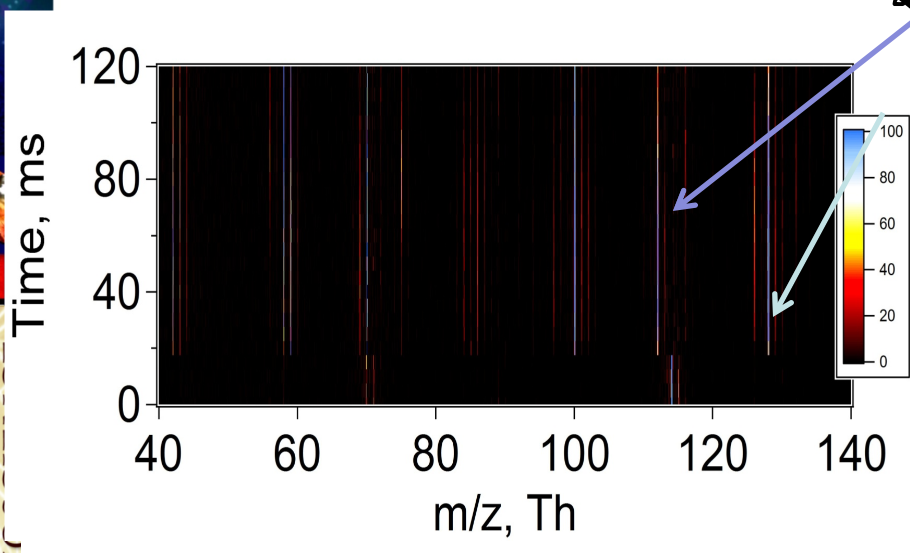
Di-isopropyl ketone oxidation shows products that are correlated with OH and HO_2 formation

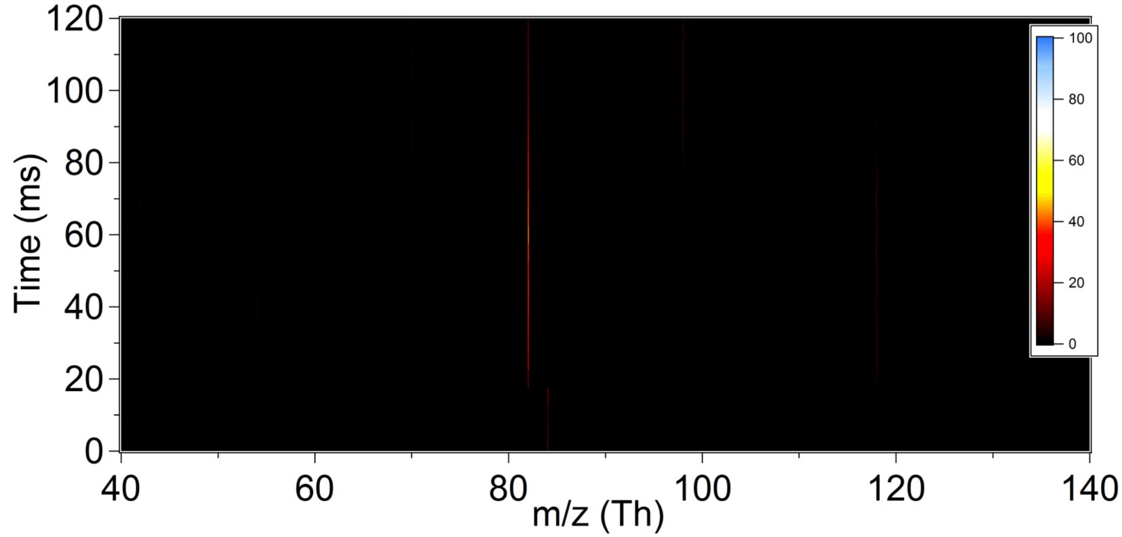




- OH formation reflects chain branching or chain propagation
- HO_2 formation is essentially chain terminating
- **Simple rule: More OH = more reactive**

Cyclopentanone (m/z=84) Chemistry is Relatively Simpler than DIK

Time-resolved product mass spectrum at 700 K (Photon energy range: 8.0 – 10.5 eV)



→ Much smaller formation of products associated with OH

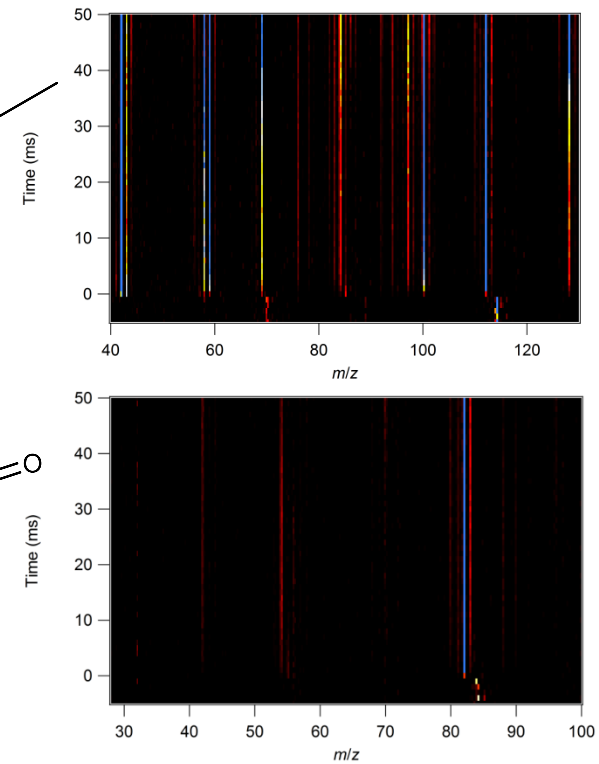
→ **But**: Still observe HO_2 elimination (strong intensity at m/z=82)

→ Applying simple rule – would predict less low- and intermediate-T reactivity than for di-isopropyl ketone

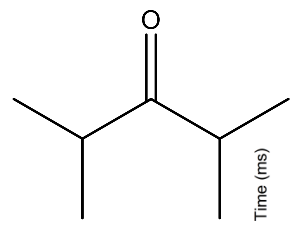
Ketone Structure Affects Reaction Pathways

- Two ketones are representative of molecular-structure effects.

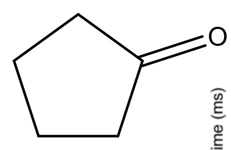
ALS Mass Spectra



- **Di-isopropyl ketone**: shows species associated with <u>chain-propagating OH formation</u>.
  - Expect intermediate temperature heat release (ITHR) in engine with associated benefits for HCCI.



- **Cyclopentanone:** shows almost exclusively cyclopentenone formation, associated with <u>chain-terminating HO_2 formation</u>.
  - Expect very little ITHR in engine.



- Engine experiments can verify the expected changes in performance with ketone structure.
- Feedback to Bio-Side for tuning production by the fungus.

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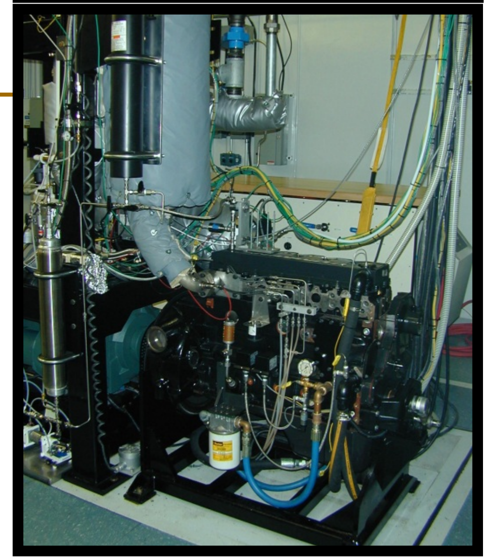
Engine Tests – Ketone Fuels

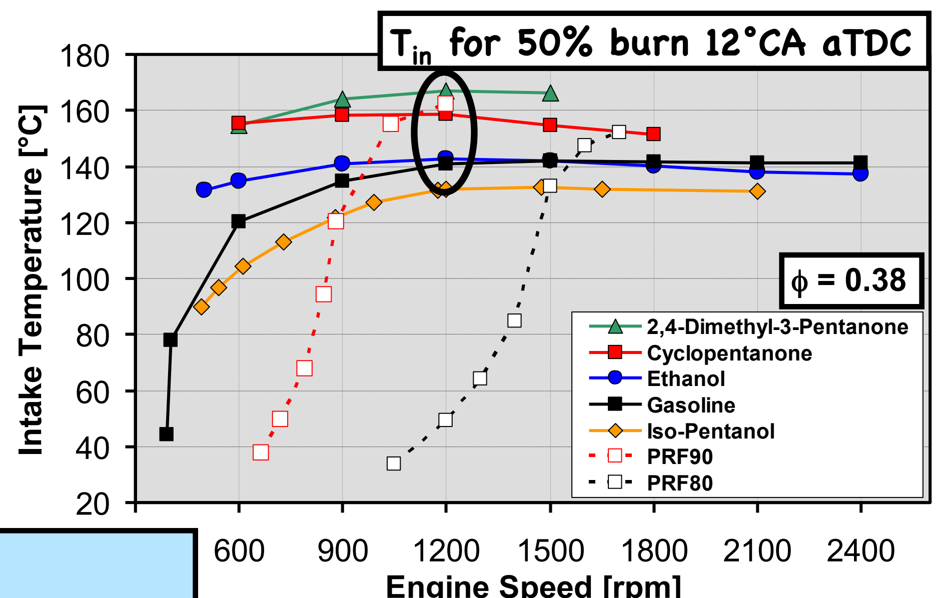
- Auto-ignition characteristics of selected Ketone fuels examined in a Homogeneous Charge Compression Ignition (HCCI) engine.
  - HCCI is an advanced IC engine combustion process that can provide high efficiency and ultra-low NO_X and particulate emissions.
  - Provides data on auto-ignition at engine time-scales and at realistic engine temperatures and pressures.
- Intake temperature (T_{in}) vs. Speed sweep characterizes overall reactivity relative to other fuels.

HCCI Research Engine



Ketone behavior is overall similar to gasoline and ethanol, but . . .

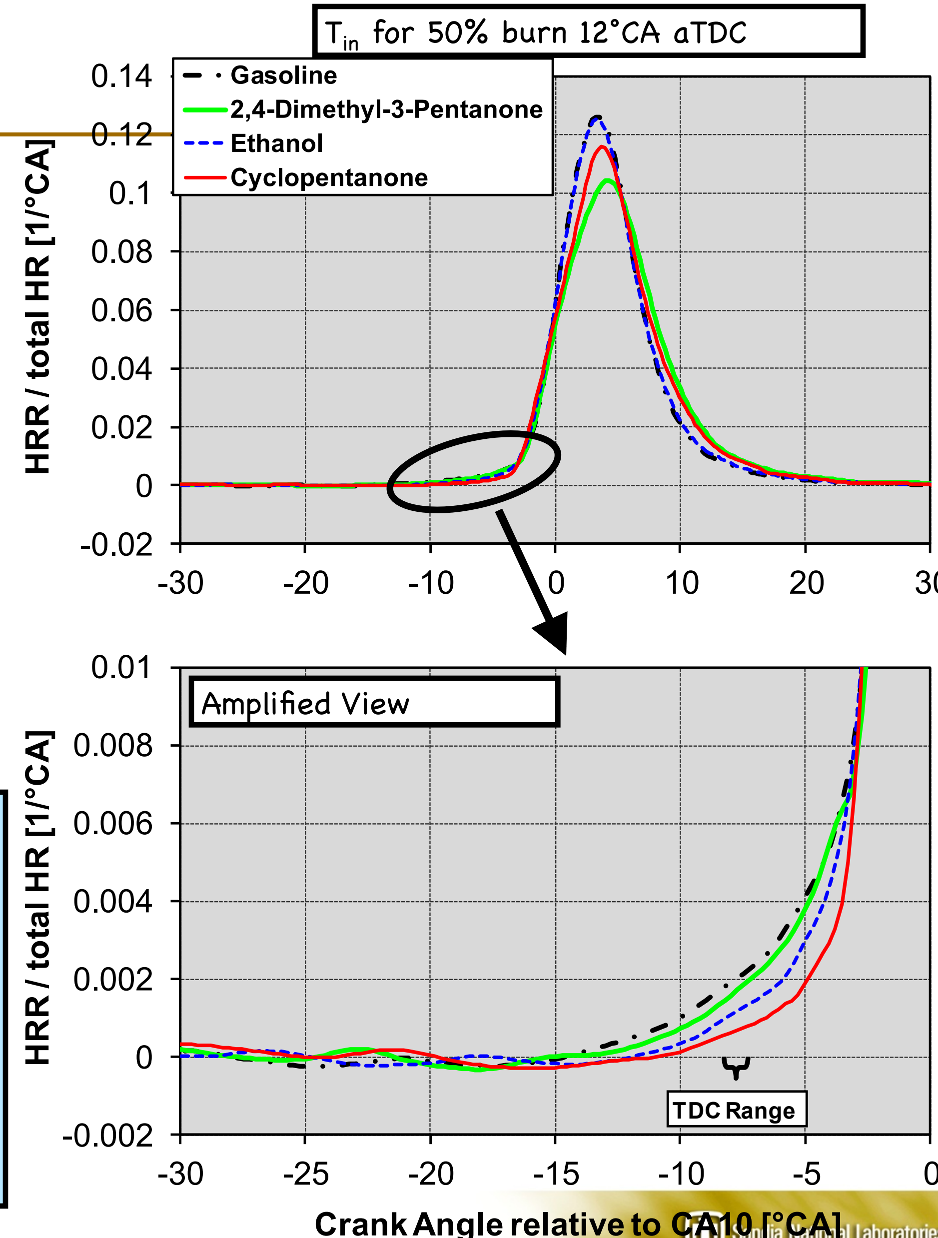
- Significantly higher T_{in} is required.
- Low-T chemistry (LTC) not significant on engine timescales.
  - PRF fuels demonstrate behavior of fuels with more LTC.



- Ketones could raise octane no. of gasoline.

Ketone Fuels Show Different Pre-Ign. Activity

- Pre-Ignition reactions are key to performance differences in fuels.
  - Low-temp. heat release (LTHR), 760 – 880 K.
  - Intermediate -temp. heat release (ITHR), 950 – 1050 K.
- Overall heat release of HCCI combustion is similar for ketones, gasoline and ethanol.
  - No LTHR at conditions studied.

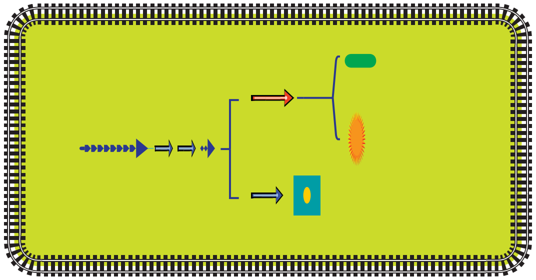


- Significant differences in ITHR.
  - For ITHR, gasoline > dimethyl-pentanone > ethanol > cyclopentanone.
  - Differences will likely affect engine performance at high loads
    - Stronger ITHR beneficial for reaching higher HCCI loads.

Rewiring Chemistry

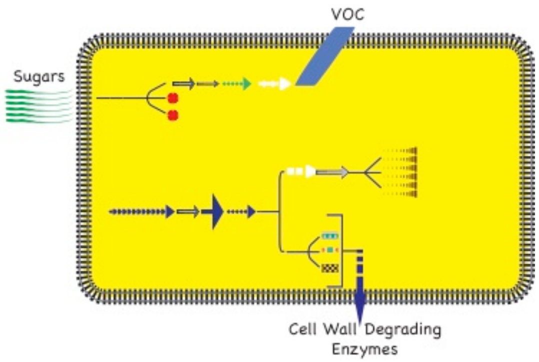
Design and Assembly for scalable production

- Toolbox to design and wire pathways for appropriate chemistry.
  - Produce and secrete cellulolytic enzymes.
  - Transport/absorb sugars and shuttle to appropriate metabolic pathway.
  - Produce VOC.



- Prototype and small-lot production.

- Develop mechanistic rules and validate.



Summary

- Identified and sequenced four fungal genomes that encode cellulolytic degradation and hydrocarbon production.
- Hydrocarbon profile is tunable.
- Ignition chemistry measurements were performed on the most abundant components (ketones and cyclic ethers).
- Engine tests were conducted using neat fuels.

- Write complex phenotype into tractable hosts.
- Develop mechanistic rules and validate.
- Small lot production and evaluation.
- Scale-up at the advanced biofuels process development unit.