



Low Temperature Heat Release Behavior of Conventional and Alternative Fuels in a Motored Engine

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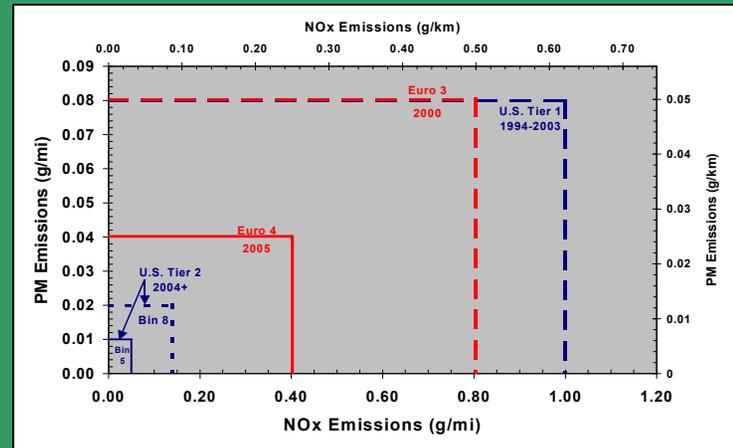


Are the growing interests in alternative diesel fuels and advanced combustion techniques compatible?

Coal-derived FT programs in PA and MT



Reduced emission standards



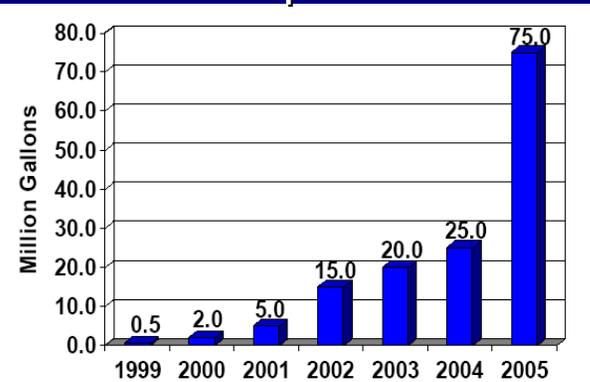
Tier 2 emission standards

Advanced combustion techniques



Reproduced from Ryan

Biodiesel production



National Biodiesel Board (nbb.org)



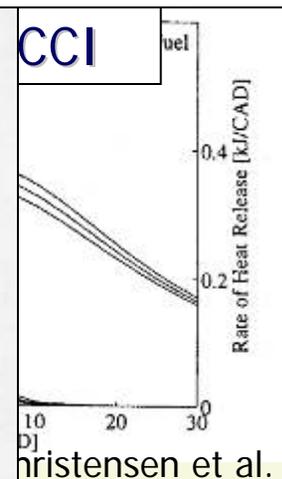
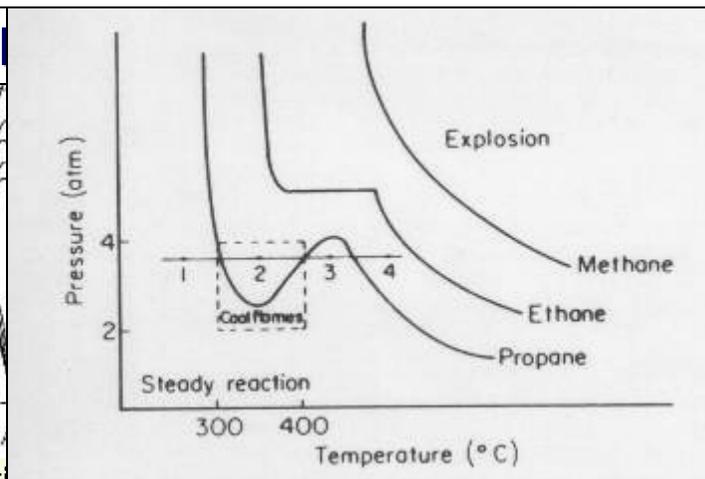
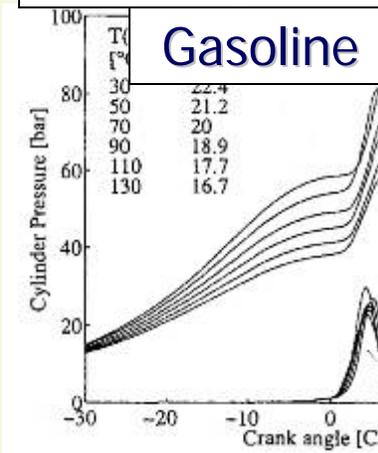
Are advanced combustion techniques sensitive to fuel composition?

...it is almost certain that future, advanced combustion engine technologies will show a greater [performance and emissions] sensitivity to [fuel-property] variations...
(section 4.7.1 of the FreedomCAR Multi-Year Program Plan)

- **Lack of direct control of combustion timing**
 - No spark initiation in most cases
 - Limited control with fuel injection timing (combustion strategy dependent)
 - Combustion is kinetically initiated
- **Traditional fuel ignition properties may not be sufficient indicators of advanced combustion performance**
 - Influence of “physical” vs. “chemical” cetane number

Low temperature heat release

With increasing temperature at constant pressure
Non-Explosive → Explosive → Non-Explosive → Explosive

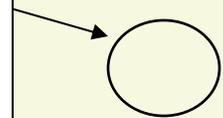


Reproduced from Christensen et al.

Christensen et al.

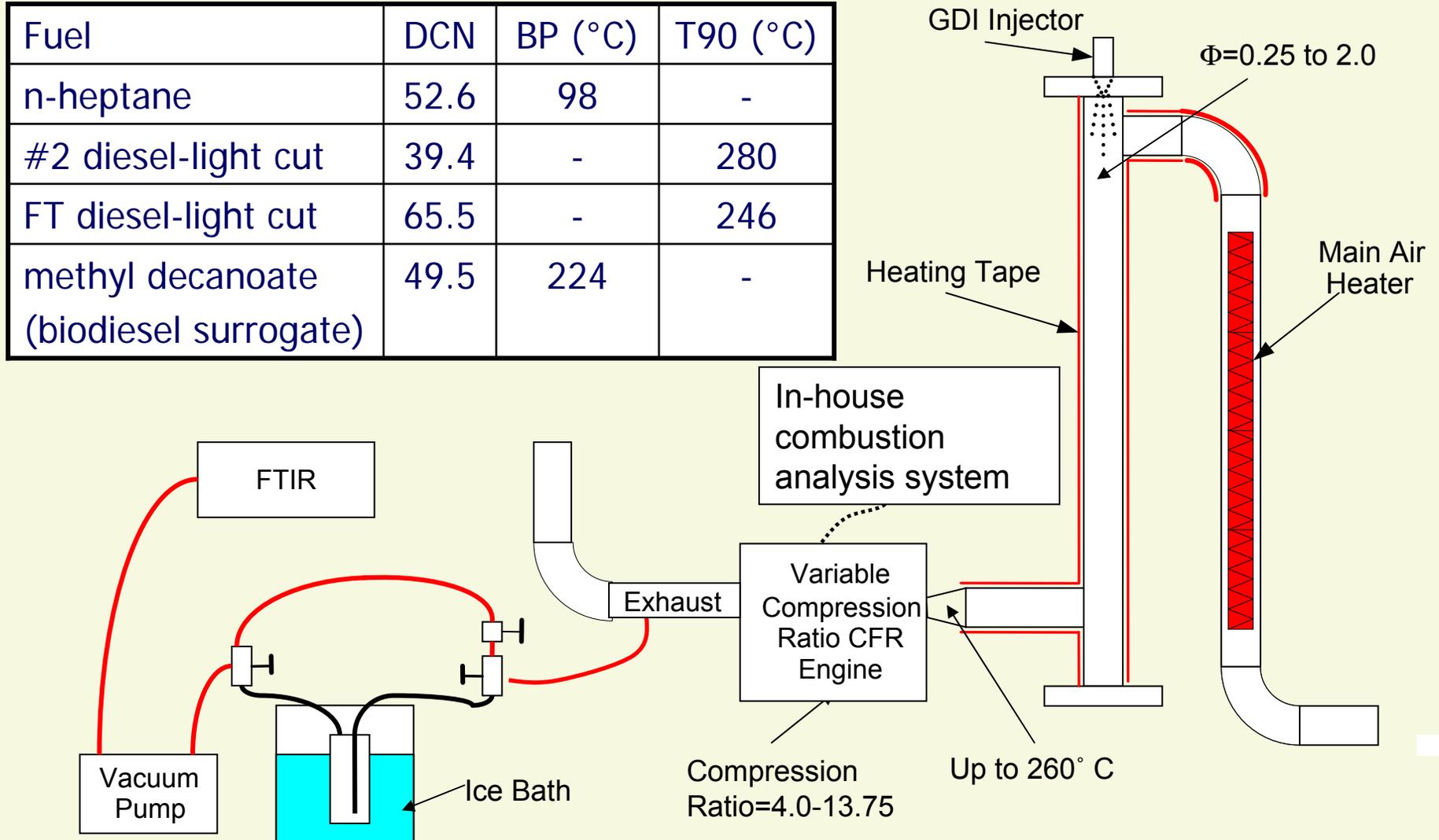
Reproduced from Glassman, 1996

- What is formed during LTHR?
- Alternative fuel differences?

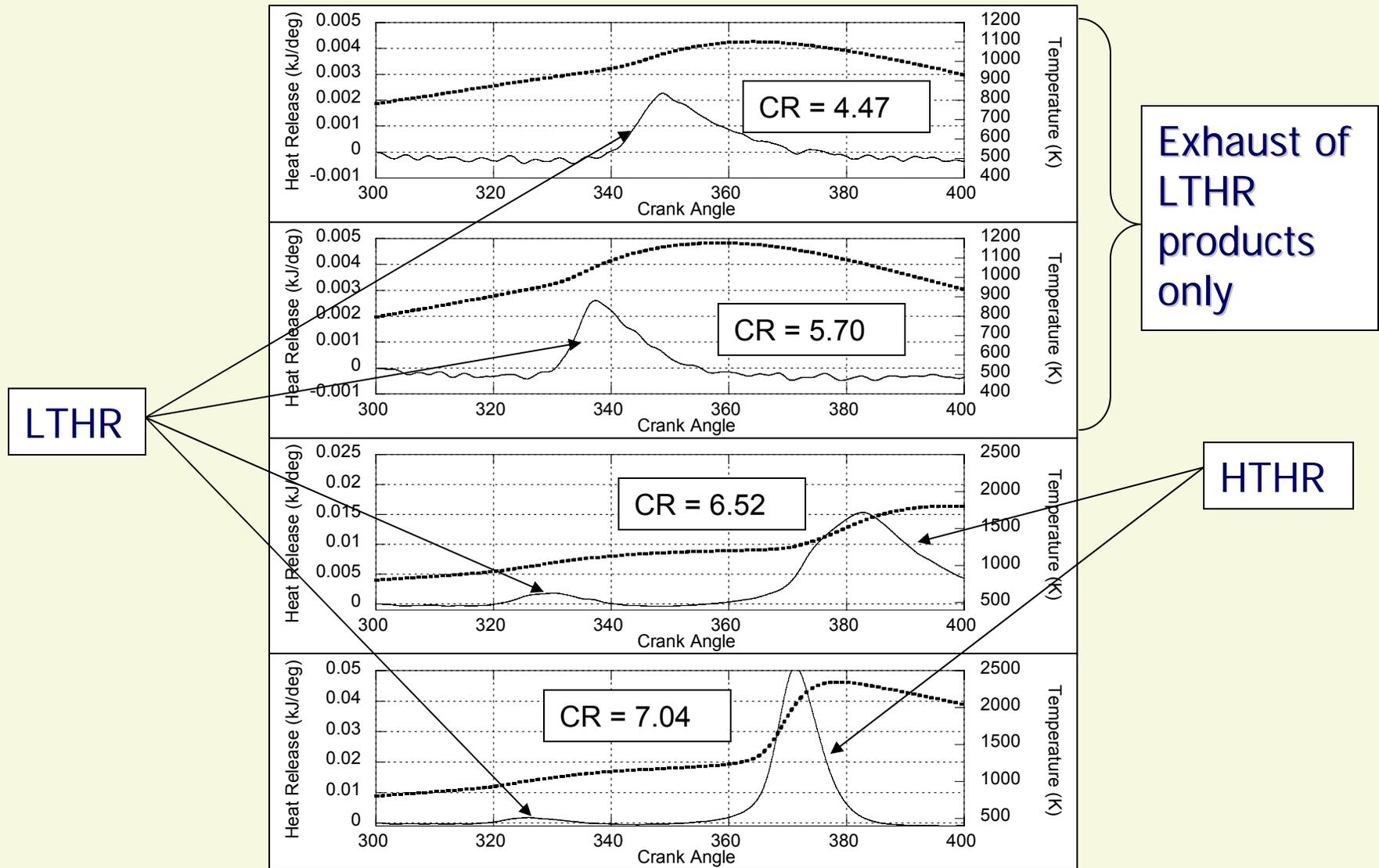


Experimental platform and fuel matrix

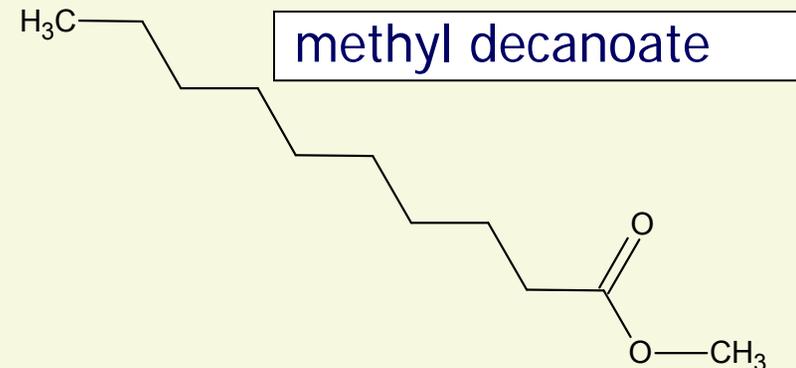
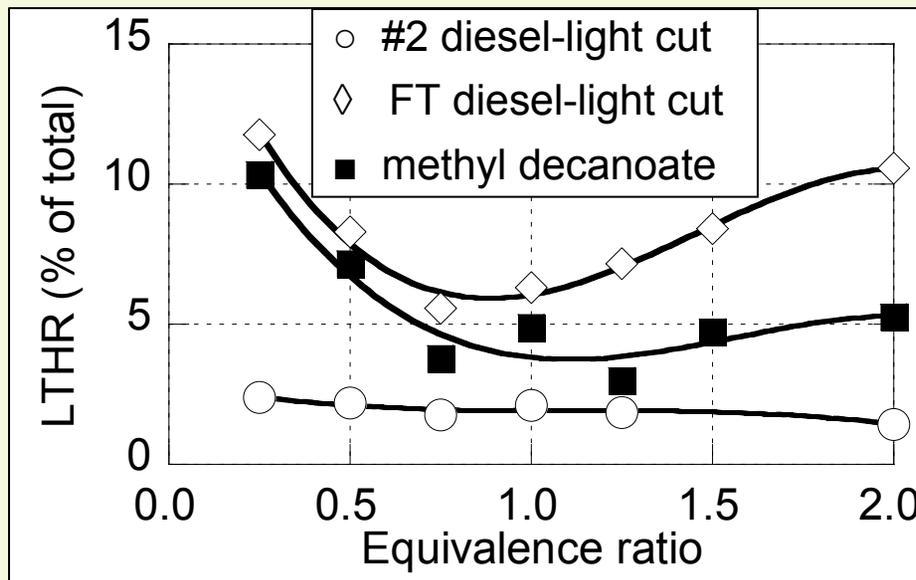
Fuel	DCN	BP (°C)	T90 (°C)
n-heptane	52.6	98	-
#2 diesel-light cut	39.4	-	280
FT diesel-light cut	65.5	-	246
methyl decanoate (biodiesel surrogate)	49.5	224	-



Fuels progressed from only LTHR at low CR to LTHR and HTHR at higher CR



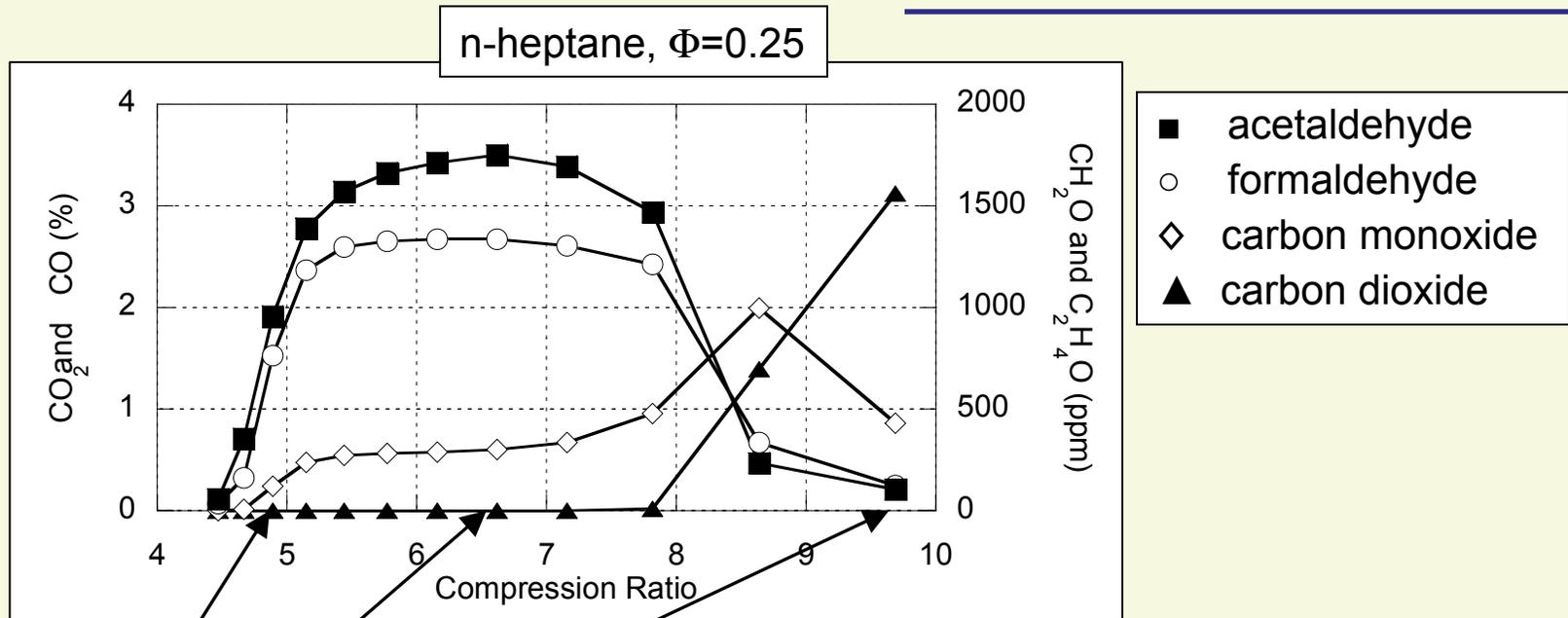
LTHR magnitude is dependent on CN and equivalence ratio



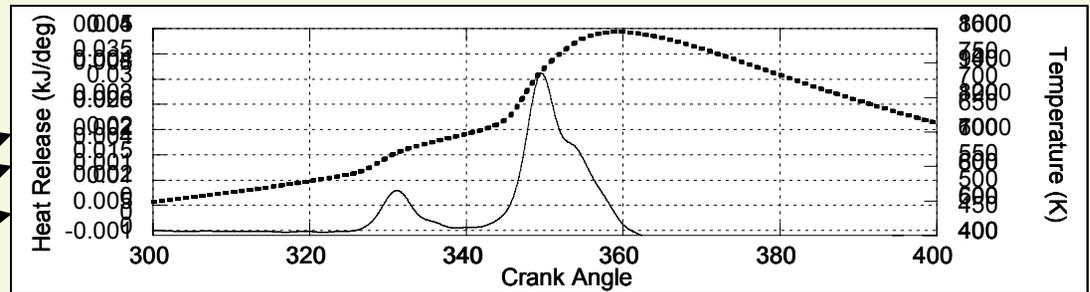
- **LTHR magnitude trends with derived cetane number**
 - FT diesel-light cut > methyl decanoate > #2 diesel-light cut
- **Methyl decanoate LTHR likely over-predicts LTHR of biodiesel**
 - Aliphatic chain is responsible for LTHR, not methyl ester
 - Over 50% of soy-based biodiesel is comprised of species with multiple unsaturations
 - Unsaturated species exhibit less LTHR than saturated species



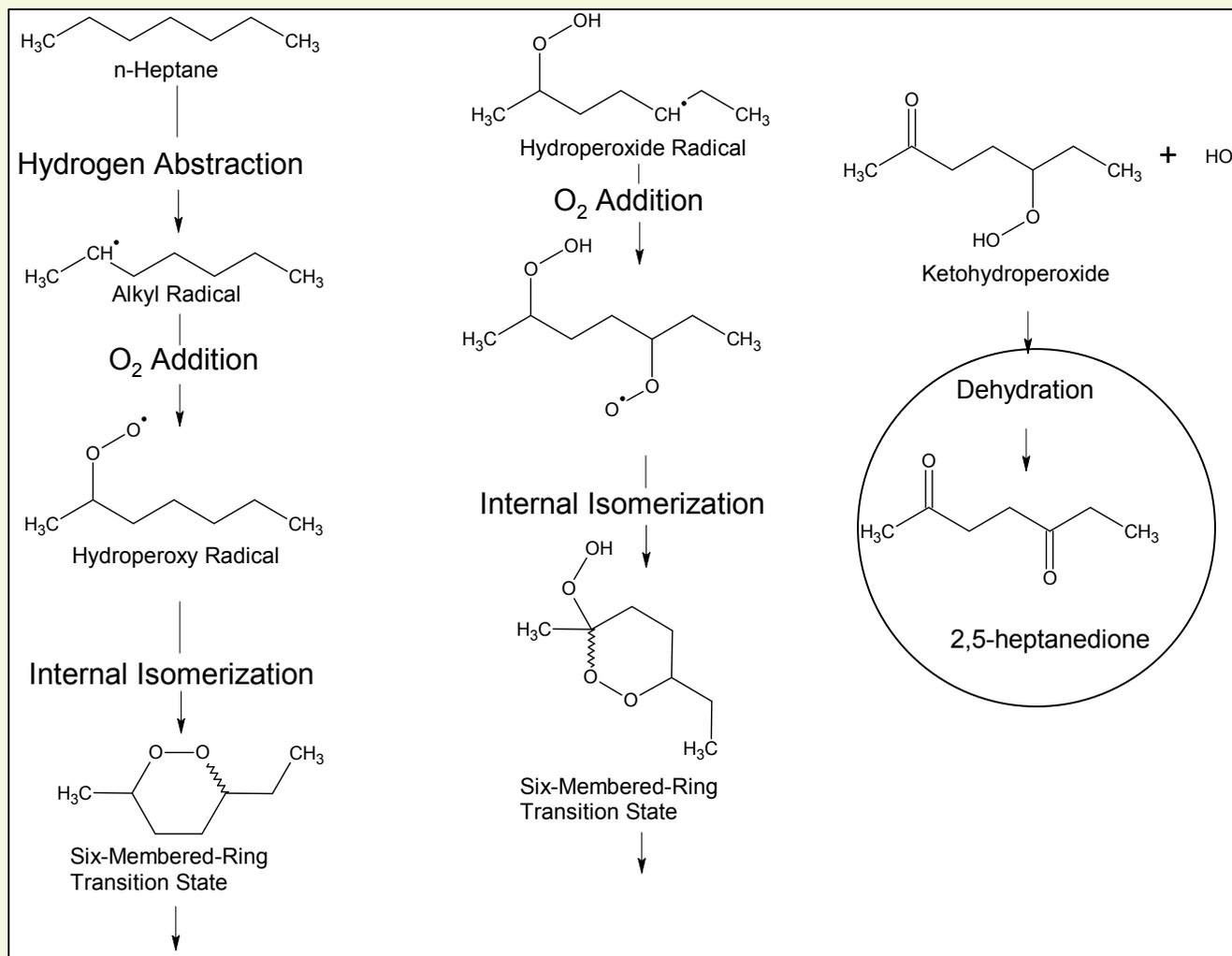
FTIR analysis of n-heptane exhaust reveals CO and aldehydes are formed by LTHR



- LTHR and not HTHR
- No reaction at low CR
- Aldehyde and CO concentrations plateau or CO
- Negligible CO_2



2,5 heptanedione identified in n-heptane exhaust condensate



Additional Species Identified

Butanal

2,3 Butanedione

4-penten-2-one

2-pentanone

Butanoic acid

Pentanoic acid

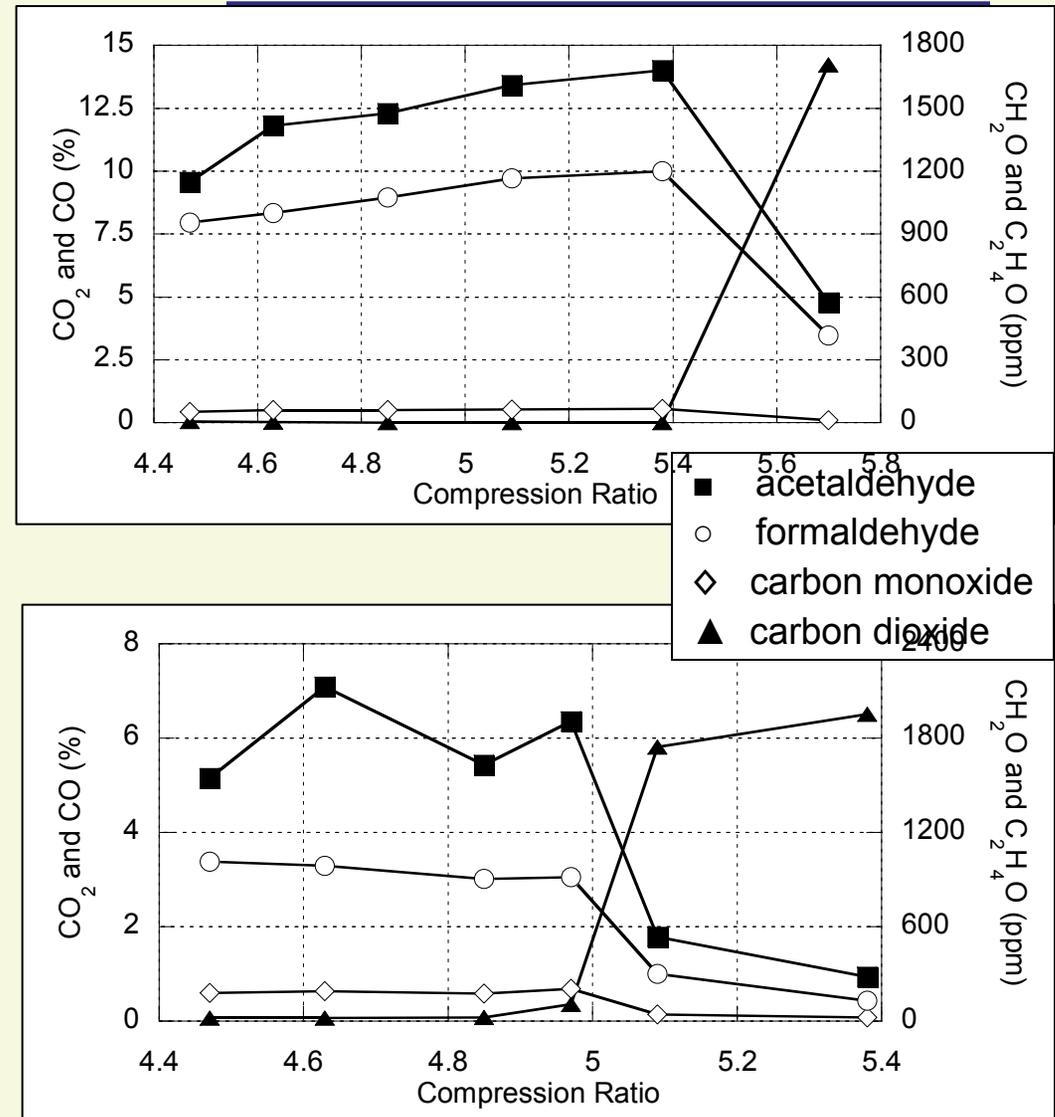
2,5 hexanedione

2-pentanone, 5-(1,2-propadienyloxy)

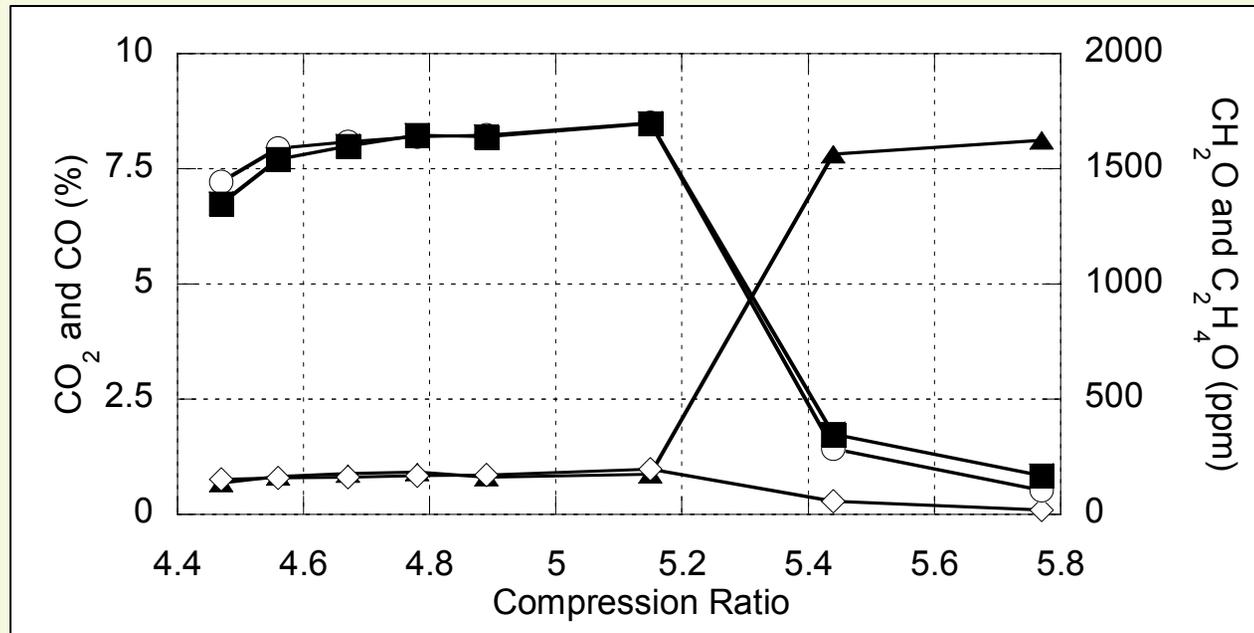
Reaction scheme taken from Curran et al., 1998.

Conventional diesel and FT fuels show trends similar to n-heptane

- Partially oxidized species are formed by LTHR, consumed by main combustion event at higher CR
- High MW oxygenated species identified in exhaust condensate
 - C7 to C15 straight-chain aldehydes
 - C9 to C12 straight-chain 2-ketones
 - C5 to C11 straight-chain organic acids

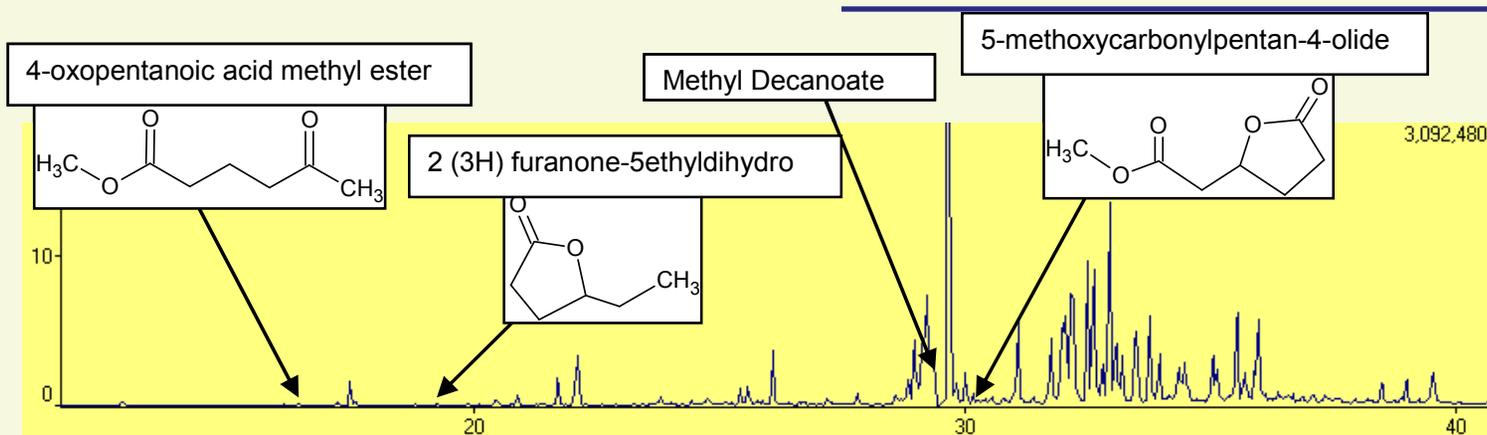


Decarboxylation of methyl decanoate produces CO₂ during LTHR



- **Comparable levels of CO and CO₂ are formed by LTHR**
 - Temperatures are insufficient to oxidize CO to CO₂
 - CO₂ is a product of decarboxylation
- **Decarboxylation is undesirable from soot-suppression standpoint**
 - Under-utilization of fuel-bound oxygen to remove carbon from soot-precursor reactions
 - Better oxygen utilization could be realized by oxygenates with ether functional groups

LTHR reactions of aliphatic chain occur prior to decarboxylation



Methyl esters	Retention Time
2-methyl butanoic acid methyl ester	12.86
Methyl hexanoate	17.45
Methyl heptenoate	17.59
Methyl octenoate	21.72
Methyl octanoate	22.06
Methyl nonenoate (isomers)	22.12, 25.85
Methyl nonanoate	25.90
Methyl decenoate (isomers)	28.83 + 4 others
methyl decanoate	29.50

Oxo-methyl ester	Retention Time
4-oxopentanoic acid methyl ester	16.45
5-oxopentanoic acid methyl ester	17.45
5-oxohexanoic acid methyl ester	20.90
6-oxoheptanoic acid methyl ester	25.44
4-oxooctanoic acid methyl ester	29.86
2-oxodecanoic acid methyl ester	30.03
9-oxodecanoic acid methyl ester	32.06



Conclusions

- **LTHR behavior of different fuels can be investigated in a motored engine**
- **LTHR magnitude trends with cetane number**
- **The oxidation taking place during LTHR produces partially oxidized species with only negligible amounts of CO₂**
 - High concentrations of CO and aldehydes
 - 2,5-heptanedione, found in n-heptane exhaust condensate, can be closely linked to LTHR mechanism
- **If allowed to proceed through HTHR, partially oxidized species largely converted to CO₂**
- **CO₂ produced during LTHR from methyl decanoate is a product of decarboxylation**
 - Decarboxylation is undesirable from a soot-suppression standpoint
 - LTHR reactions with aliphatic chain can occur before decarboxylation, incorporating additional oxygen into the molecule



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