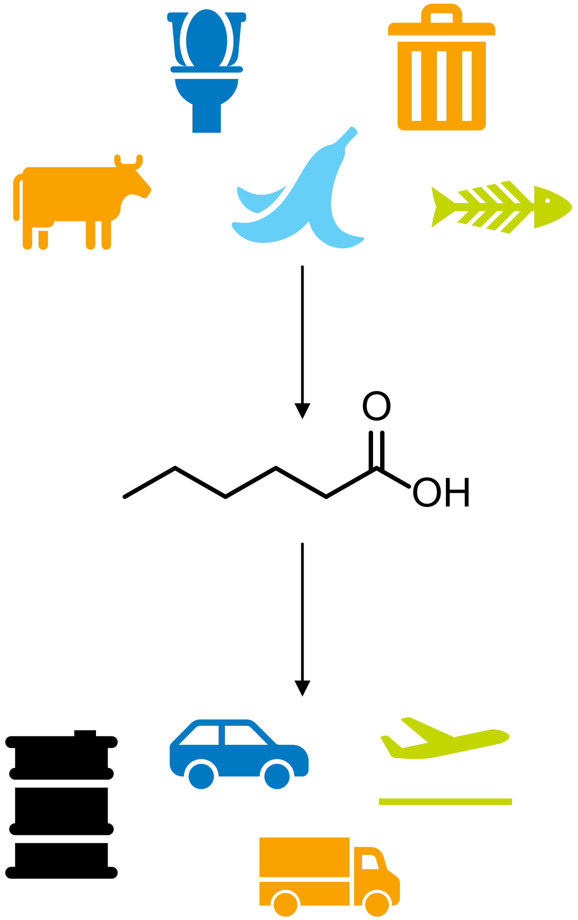
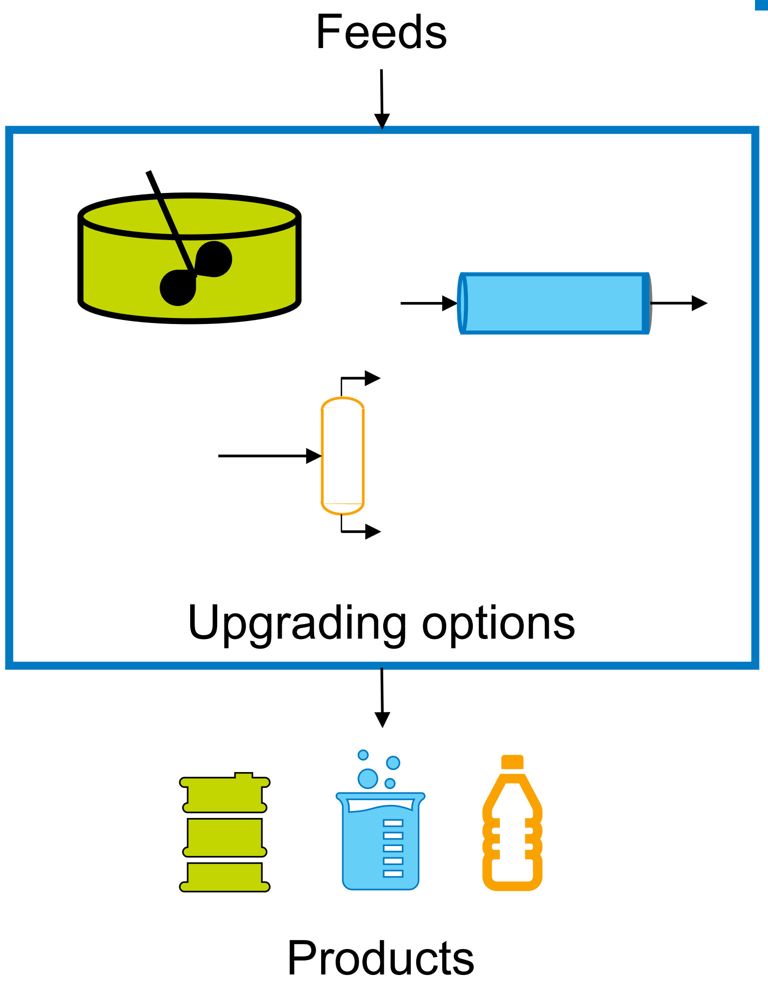
Simulation and Optimization of Volatile Fatty Acid Upgrading Strategies for Sustainable Transportation Fuel Production

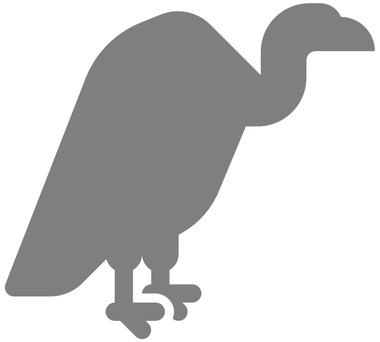
Jacob Miller,[1] Stephen Tifft,[1] Matthew Wiatrowski,[1] Pahola T. Benavides,[2] Nabila Huq,[1] Earl Christensen,[1] Teresa Alleman,[1] Cameron Hays,[1] Jon Luecke,[1] Violeta Sànchez i Nogué,[1] Eric Karp,[1] Troy Hawkins,[2] Avantika Singh,[1] and Derek Vardon[1]
[1]National Renewable Energy Laboratory, Golden, CO; [2]Argonne National Laboratory, Lemont, IL

November 15, 2022
2022 AIChE Annual Meeting, Phoenix, AZ

(i) Best liquid transportation fuels we can make with wet waste-derived volatile fatty acids (VFAs)?





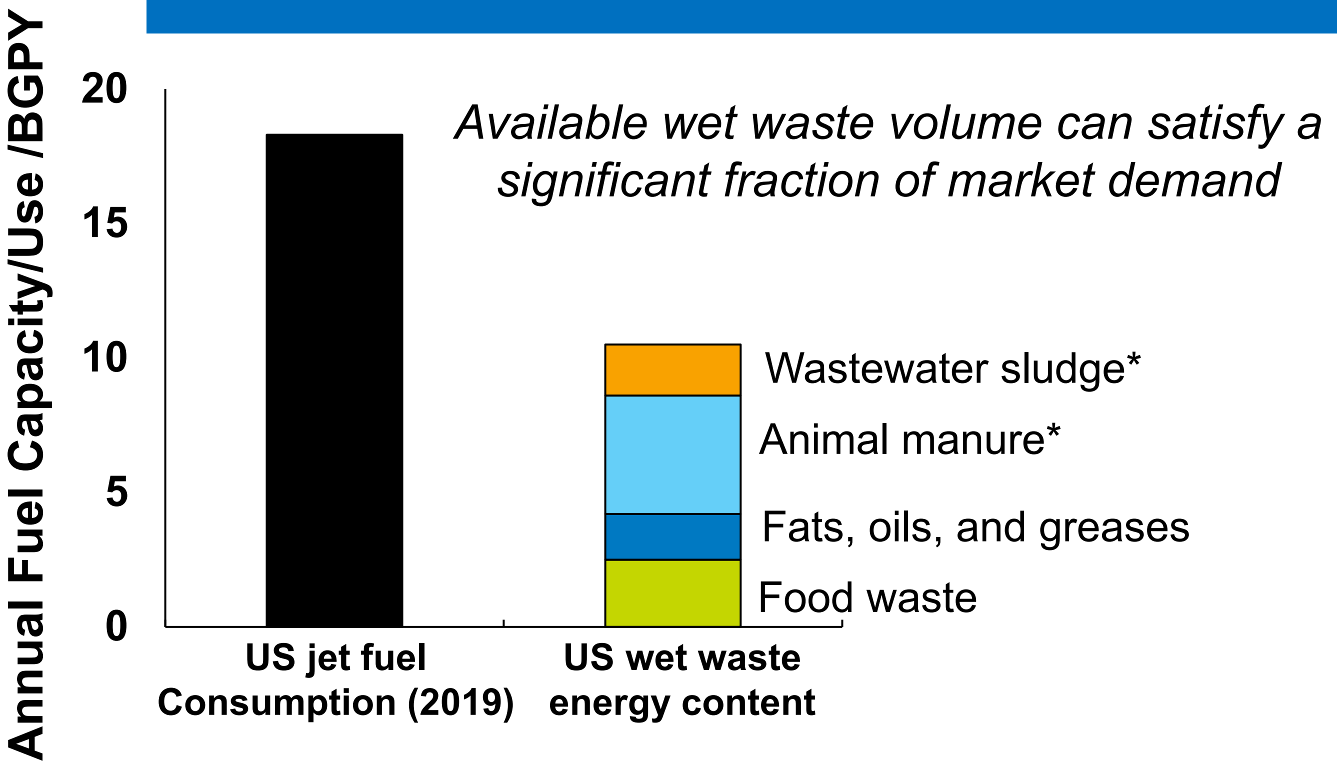


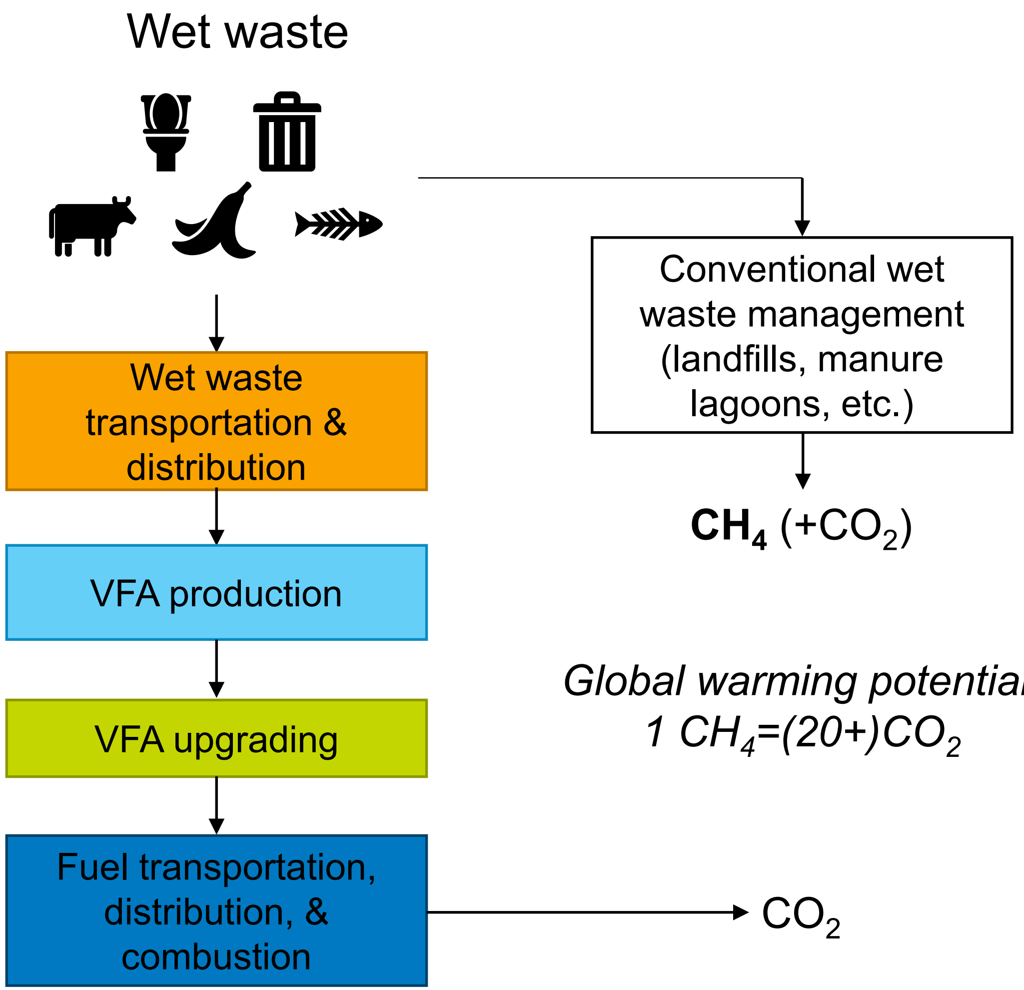
VFA Upgrading to Liquid Transportation fUels Refinery Estimation

(ii) Rapidly select “best” process topology from defined set of options?

Miller et al. *iScience* (2022) Accepted.

Wet waste utilization: Two birds with one stone?





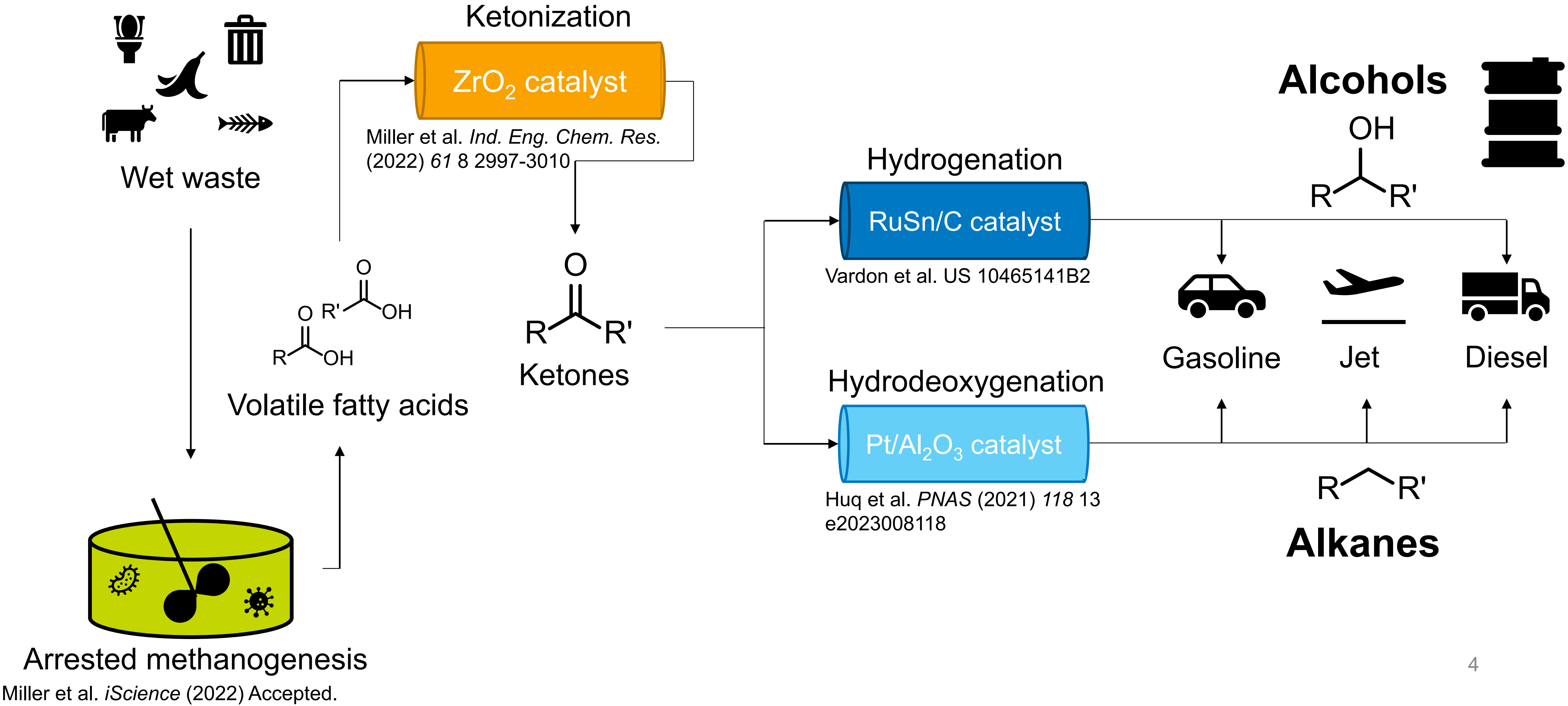
Global warming potential:
1 CH_4=(20+)CO_2

Wet waste→VFAs→fuels ***avoids CH_4 emissions****-generating conventional wet waste disposal (tradeoff: extra energy input); potential for* ***net negative GHG emissions fuels***

Skaggs et al. *Renewable and Sustainable Energy Reviews* (2018) *82*, 2640-2651.
U.S. Bureau of Transportation Statistics (2022).
Miller et al. *iScience* (2022) Accepted.

*More R&D needed to generate VFAs from these wastes

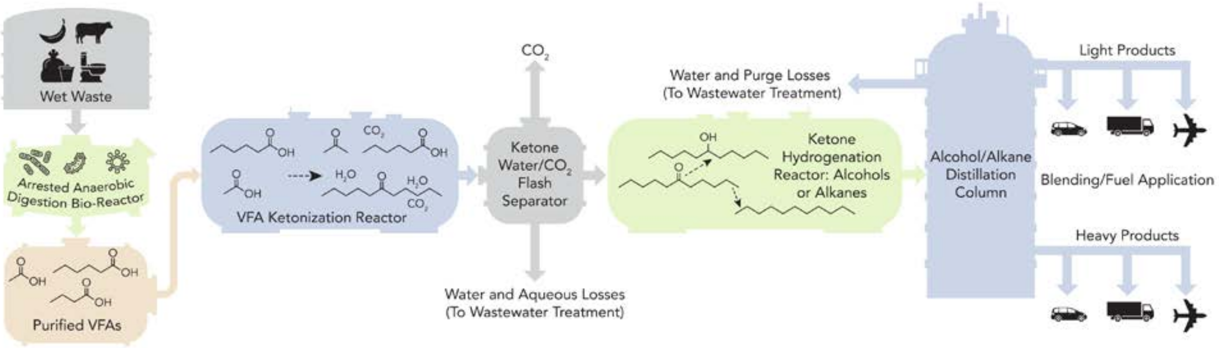
Target product: Liquid transportation fuels



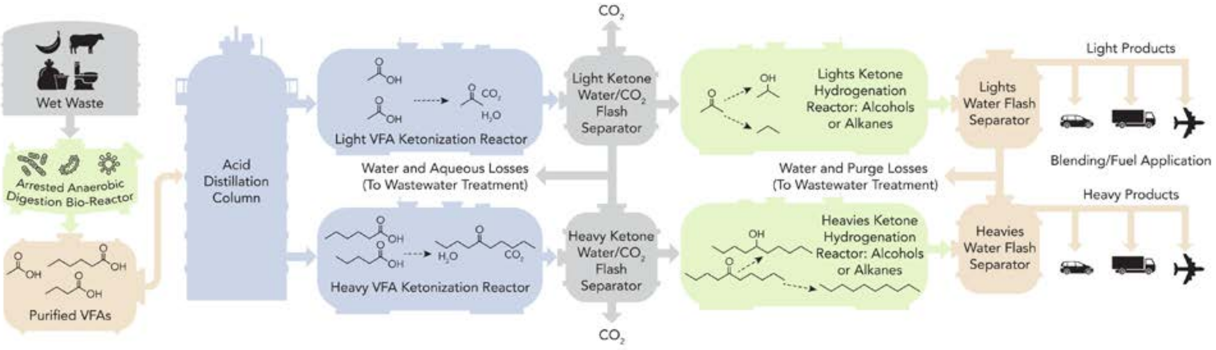
Even “simple” processes yield many operating choices

Process topology?

Process configuration #1



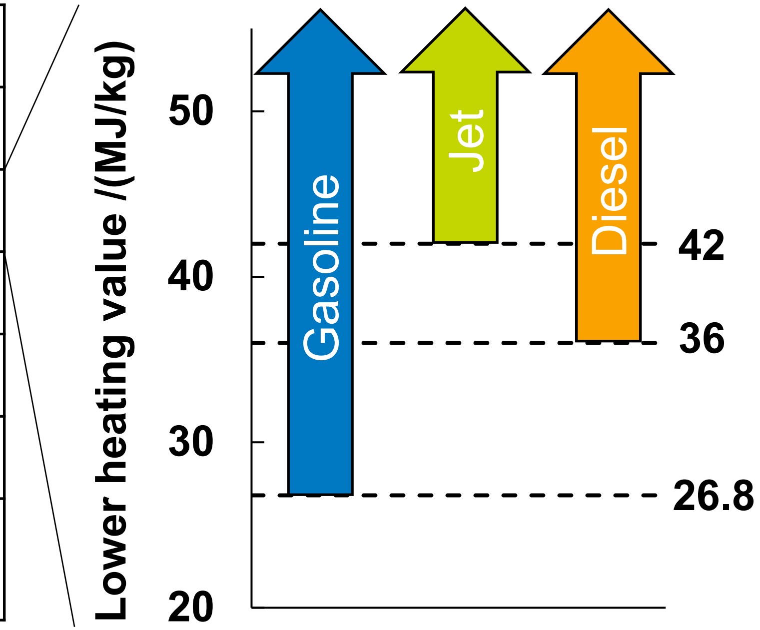
Process configuration #2



Neat biofuel? Blendability in petrofuels?

Critical fuel properties

Boiling Point
Flash Point
Lower Heating Value
Viscosity
Melting Point
Water Solubility
Cetane/Research Octane Number



Objective function defines goals

What might we want to optimize?

- High profit
- High fuel yield
- Low greenhouse gas emissions

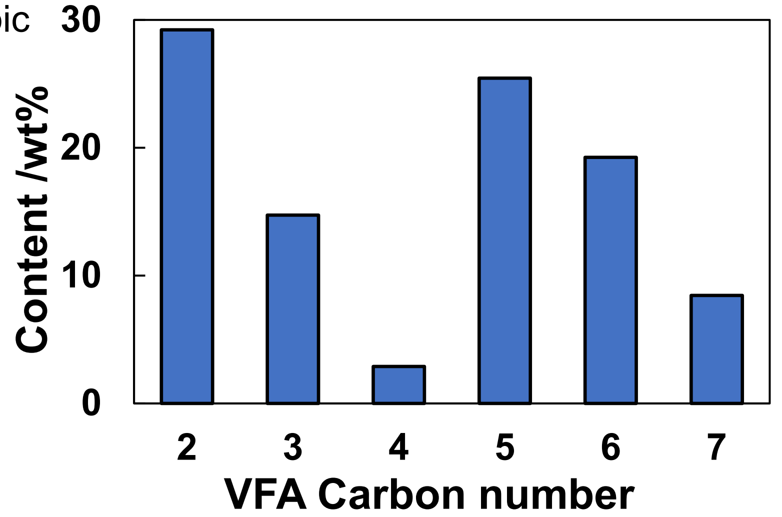
We choose biocontent (BC):

$$BC = w_1 b_1 + (1 - w_1) b_2$$

- w_1: Weight fraction of upgraded product to fuel application 1
- $b_{1,2}$: Weight fraction of fuels 1,2 that is bio-derived

VULTURE in action

VFA profiles from experimental anaerobic digestion of slaughterhouse wastes…



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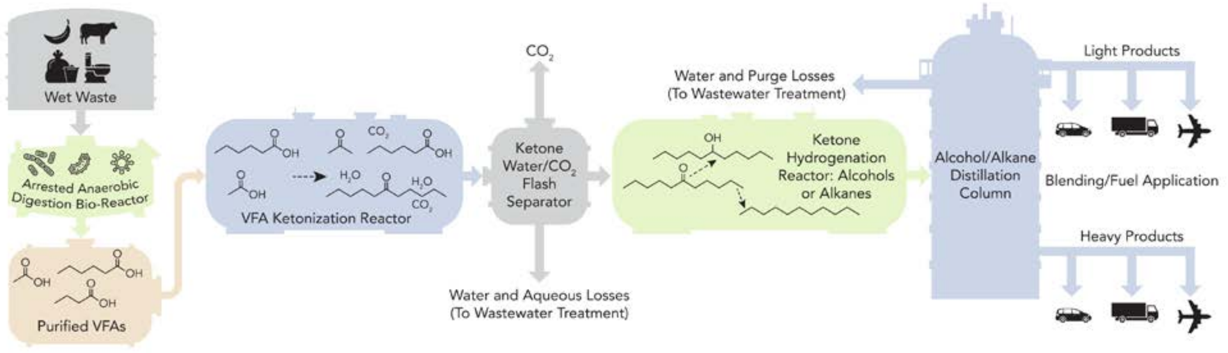
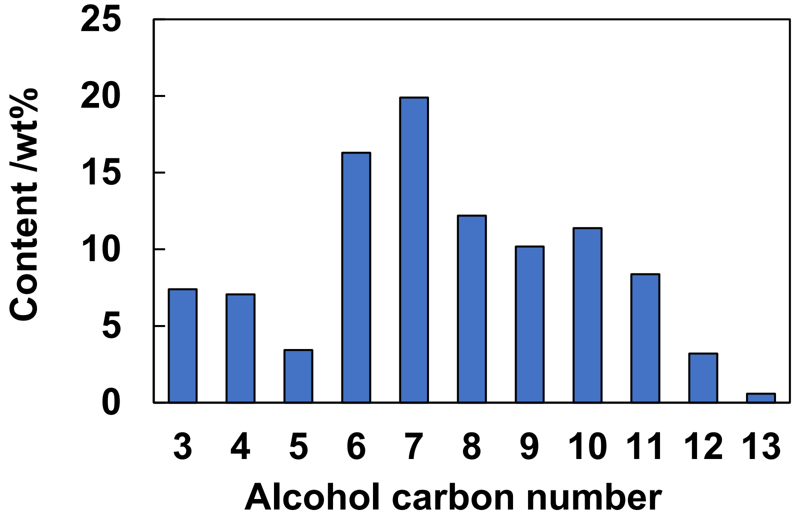


Simulated upgrading via process configuration #1, make alcohols



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Huq et al. *PNAS* (2021) *118* 13 e2023008118
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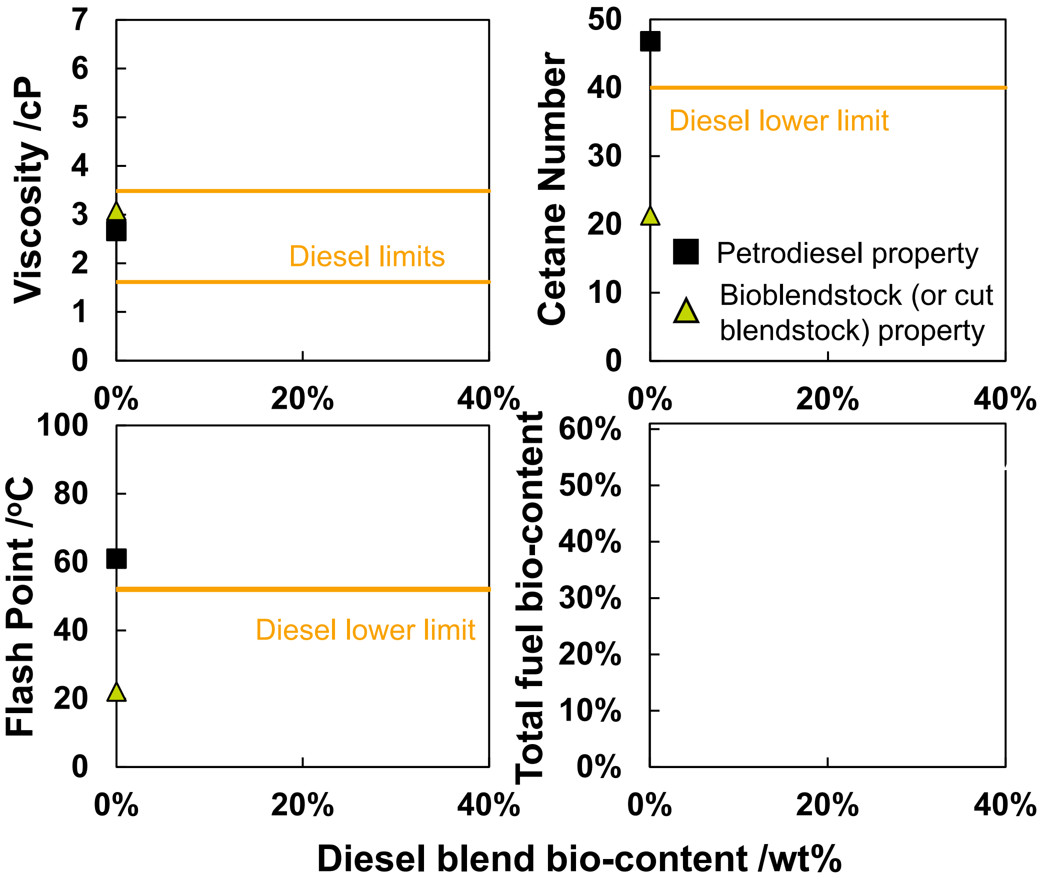
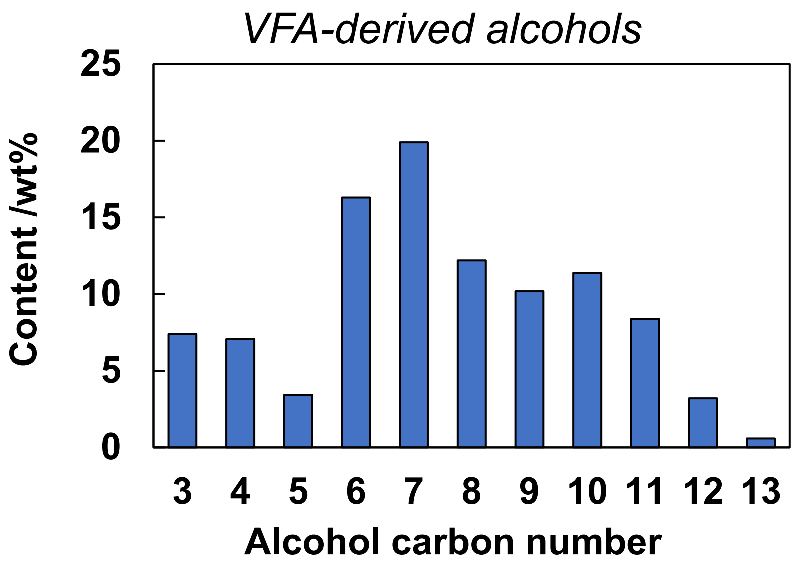
VULTURE in action: Determining optimal blending/separation





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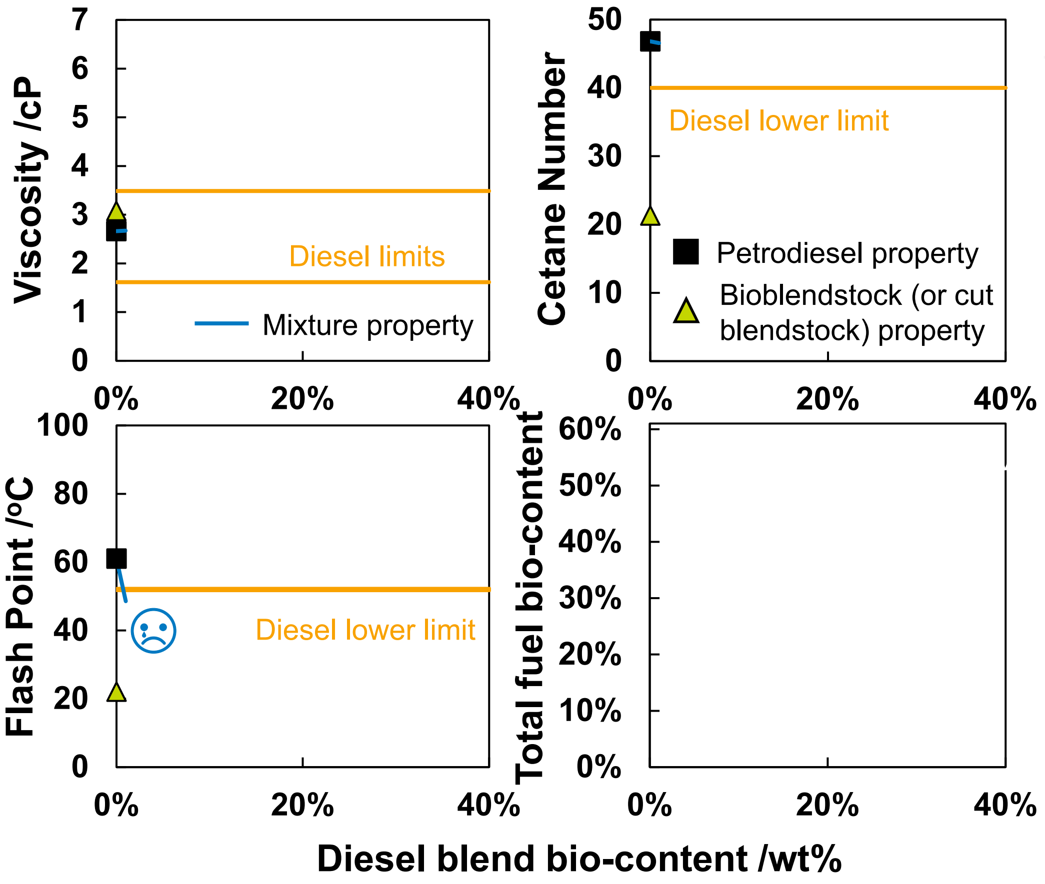
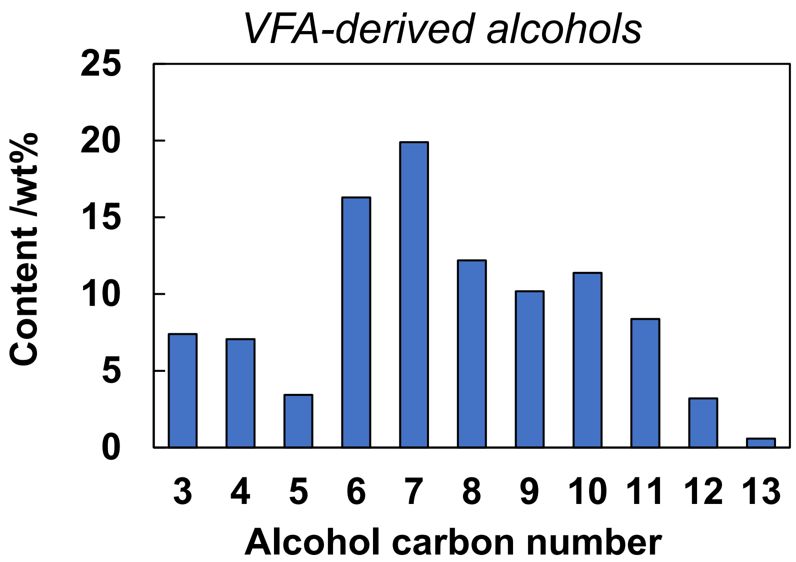


Cut	Lights	Heavies	Biocontent
0	-	Diesel, 0% (low FP)	0%



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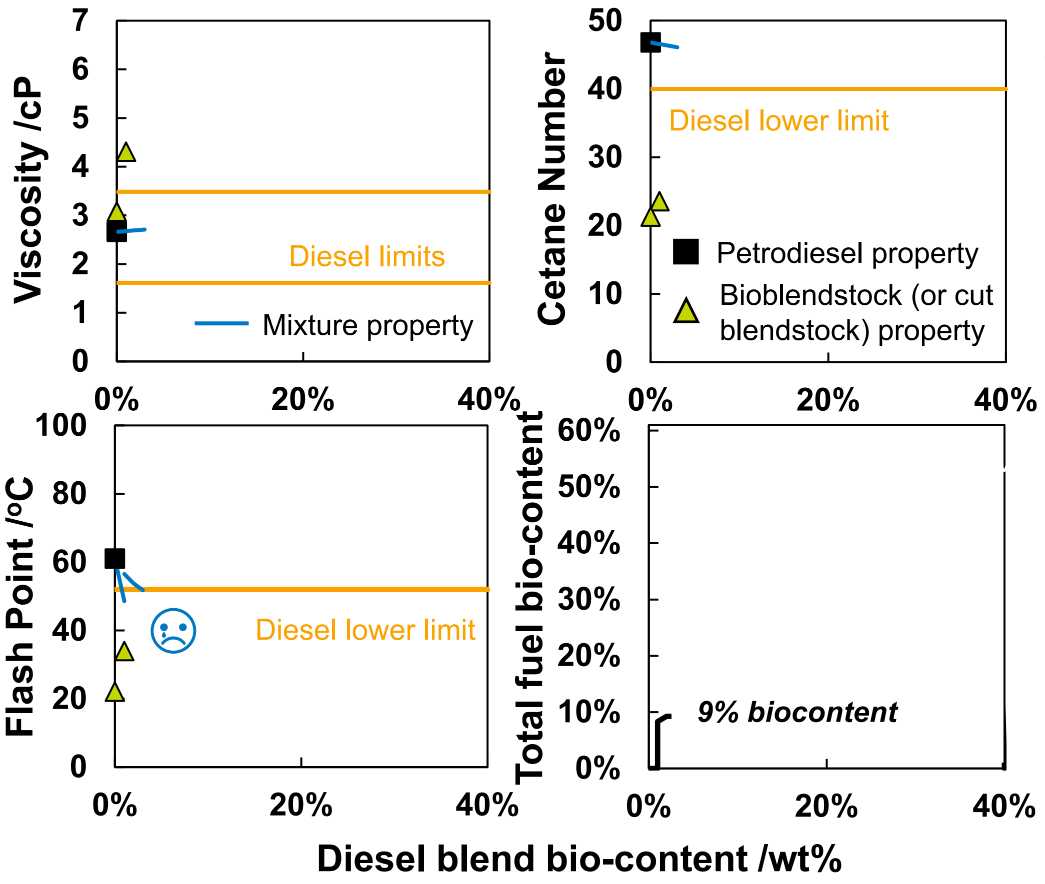
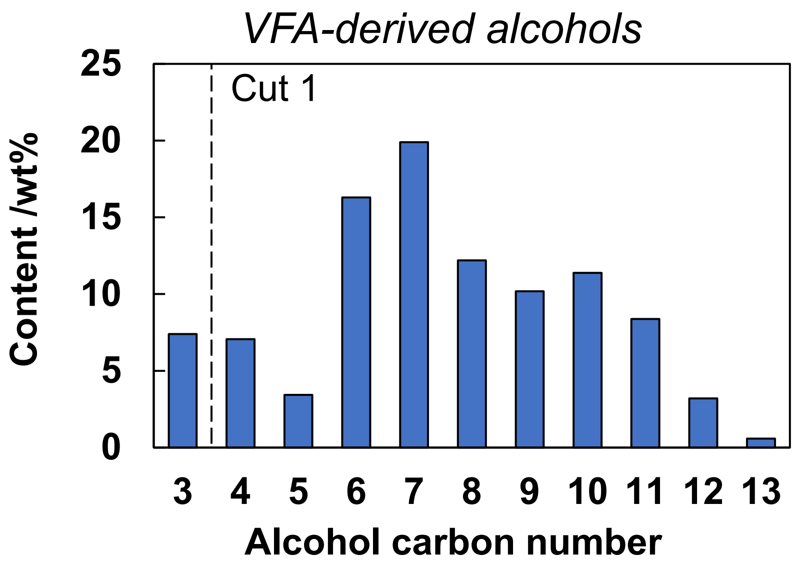


Cut	Lights	Heavies	Biocontent
0	-	Diesel, 0% (low FP)	0%
1	Gasoline, neat	Diesel, 2% (low FP)	9%



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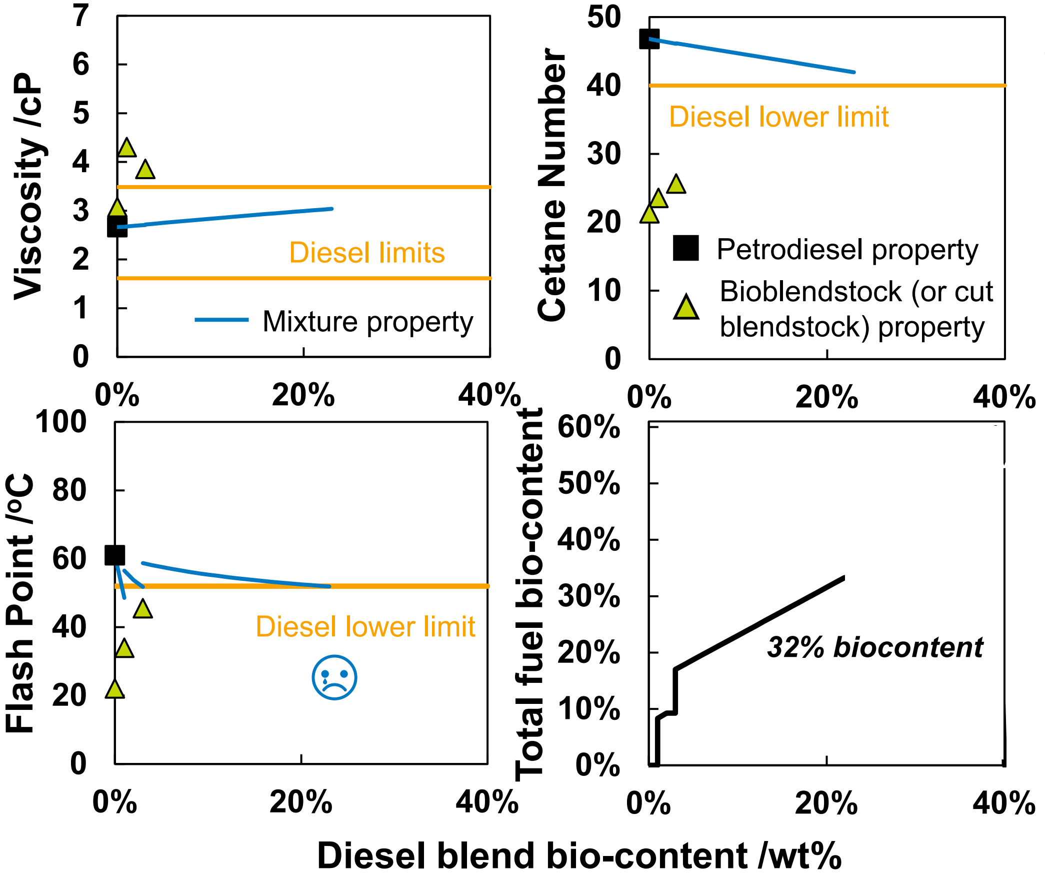
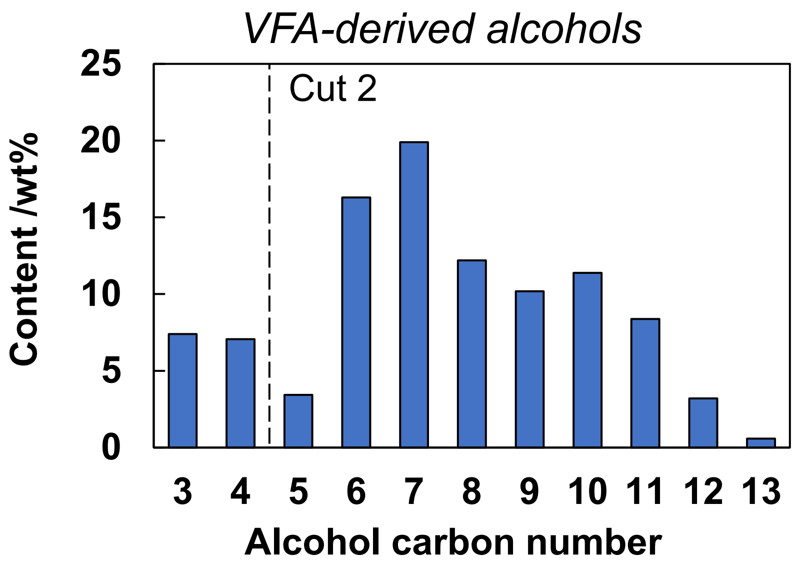


Cut	Lights	Heavies	Biocontent
0	-	Diesel, 0% (low FP)	0%
1	Gasoline, neat	Diesel, 2% (low FP)	9%
2	Gasoline, neat	Diesel, 22% (low FP)	32%



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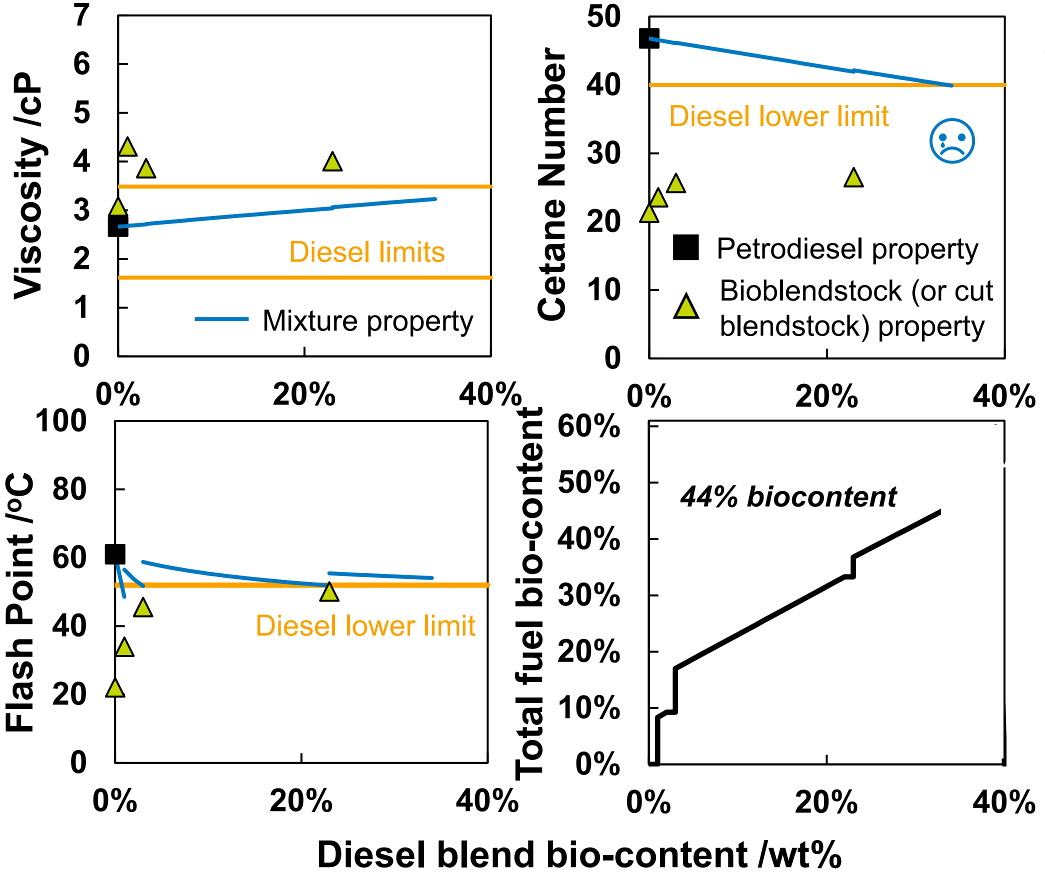

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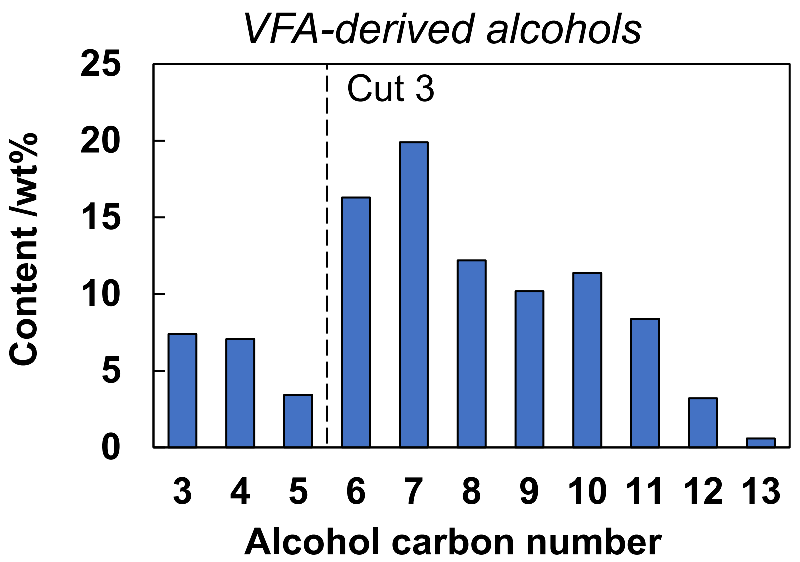
2	Gasoline, neat	Diesel, 22% (low FP)	32%
3	Gasoline, neat	Diesel, 34% (low CN)	44%



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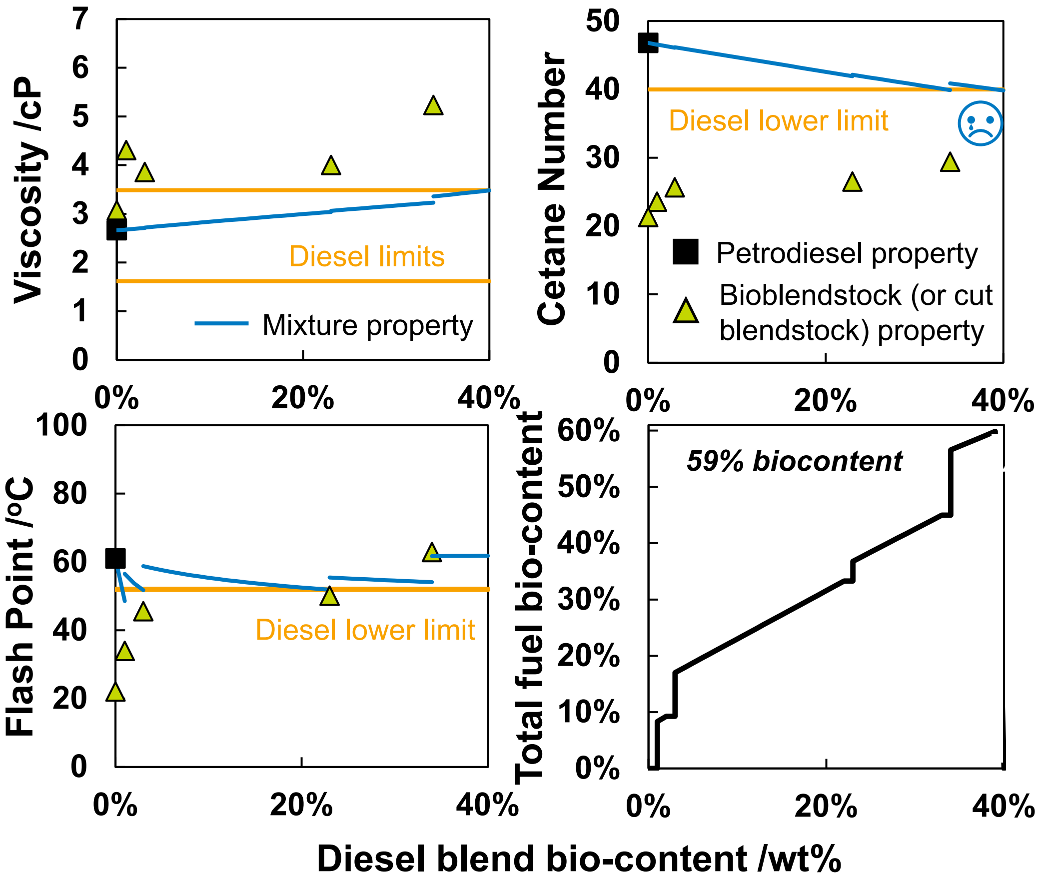

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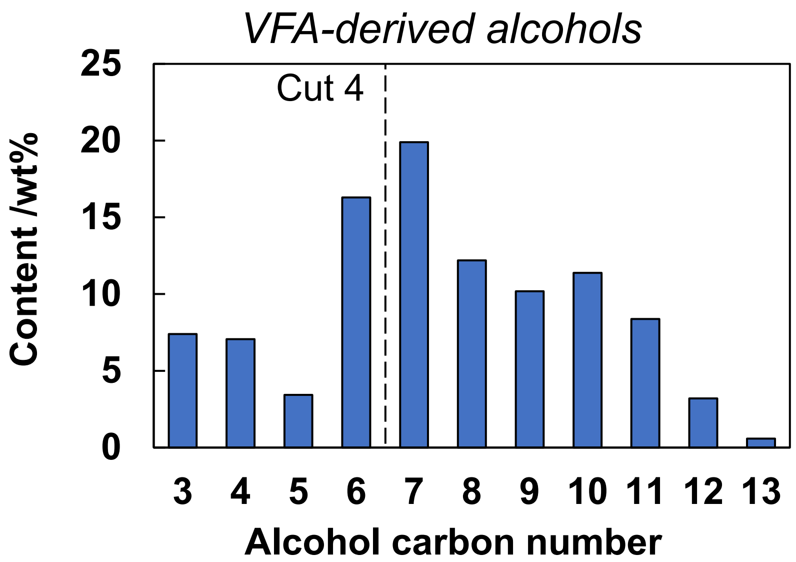
3	Gasoline, neat	Diesel, 34% (low CN)	44%
4	Gasoline, neat	Diesel, 39% (low CN)	59%



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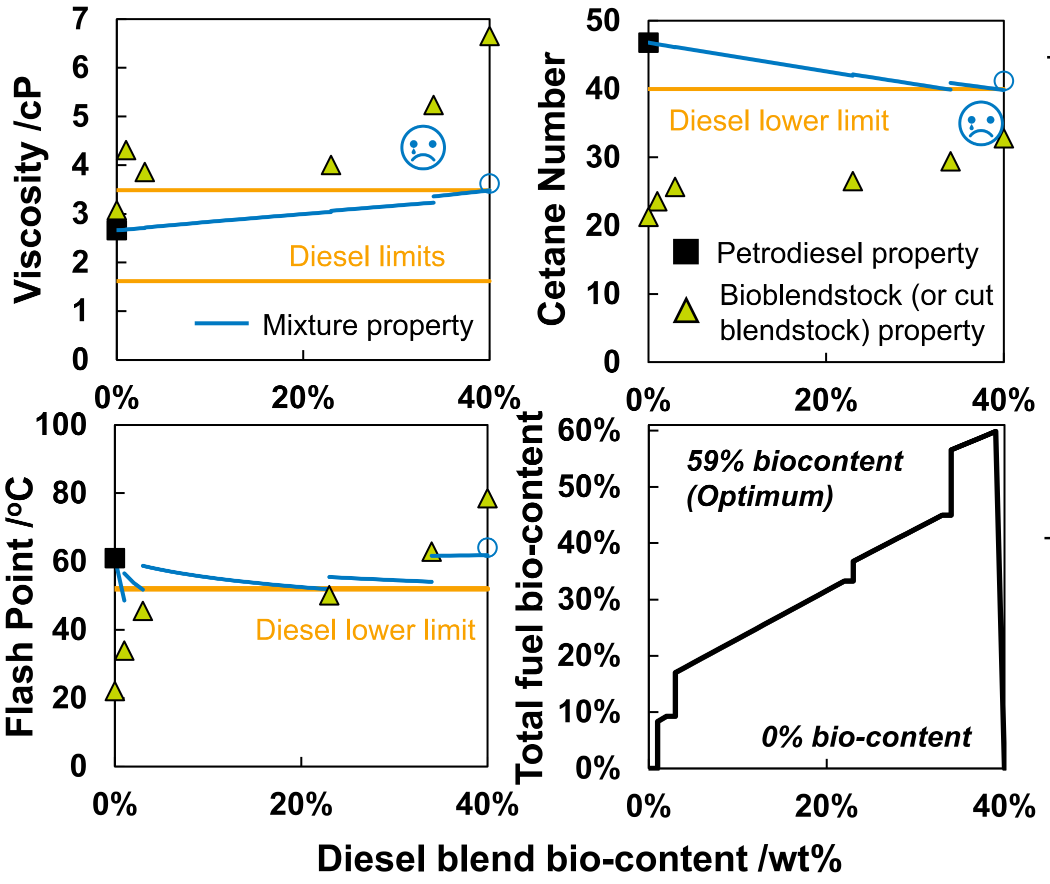

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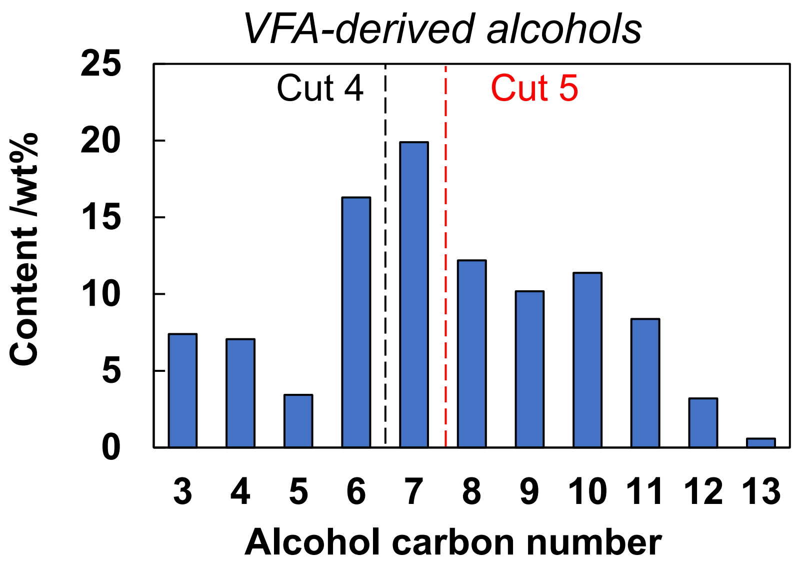
3	Gasoline, neat	Diesel, 34% (low CN)	44%
4	Gasoline, neat	Diesel, 39% (low CN)	59%
5	Gasoline, 0% (low RON)	Diesel, 0% (high viscosity)	0%



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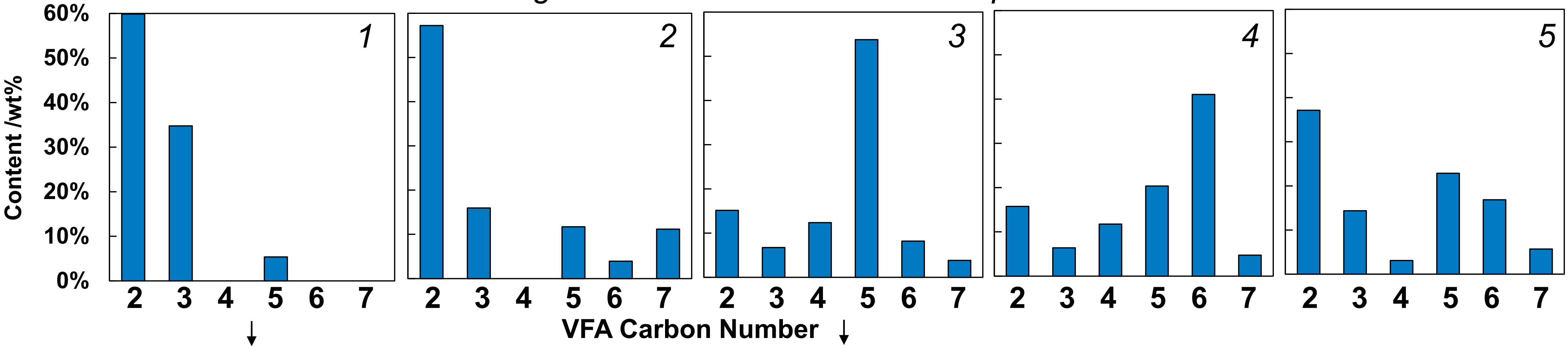
VFA to transportation fuel case studies

Slaughterhouse waste-derived VFA profiles



Mixture 1 highest-BC case (total: 100%):

100%  Neat alcohol ($C_{3\text{-}9}$) gasoline

Mixture 3 highest-BC case (total: 99%):

23%  Neat alcohol ($C_{3\text{-}7}$) gasoline

- *Most* VFA mixtures best utilized to make two separate fuels (gasoline+diesel or jet)
- When choosing between (alkane) jet fuel, alkane diesel, or alcohol diesel, heavy (C_{5+}) VFAs best utilized as jet blendstocks

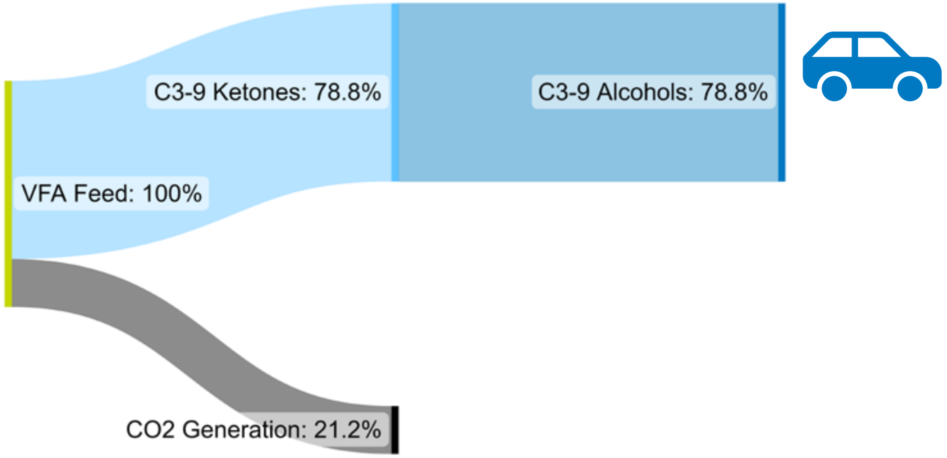
Miller et al. *iScience* (2022) Accepted.

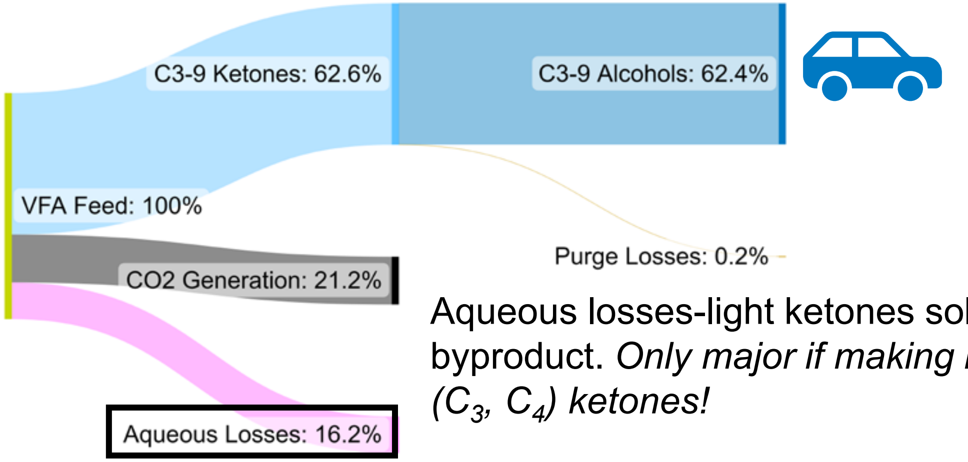
Simple process assumptions *mostly* accurate for carbon flows

VULTURE assumptions: No separations non-idealities

Aspen Plus model: Incorporate non-idealities

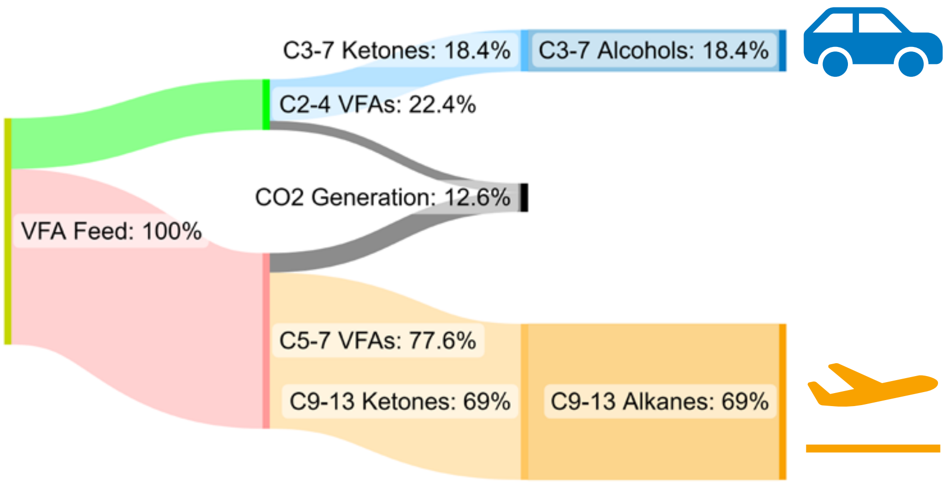
Mixture 1 highest-BC case

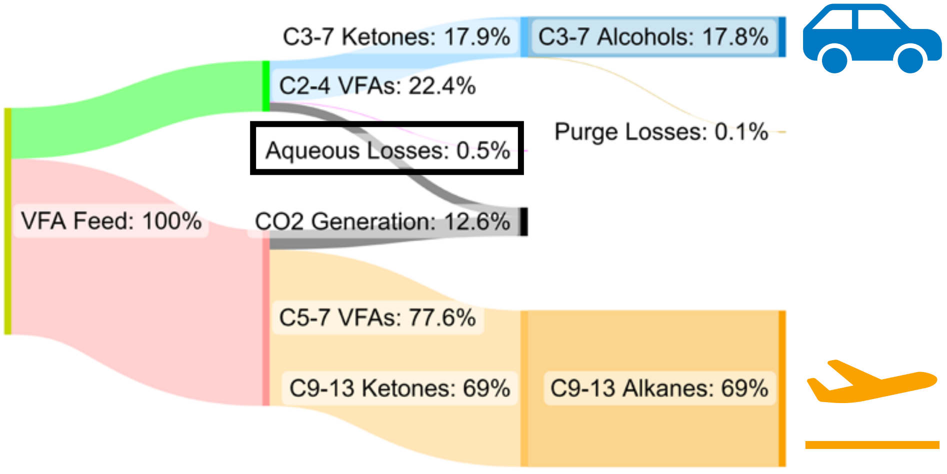




Aqueous losses-light ketones soluble in water byproduct. *Only major if making lots of light (C_3, C_4) ketones!*

Mixture 3 highest-BC case

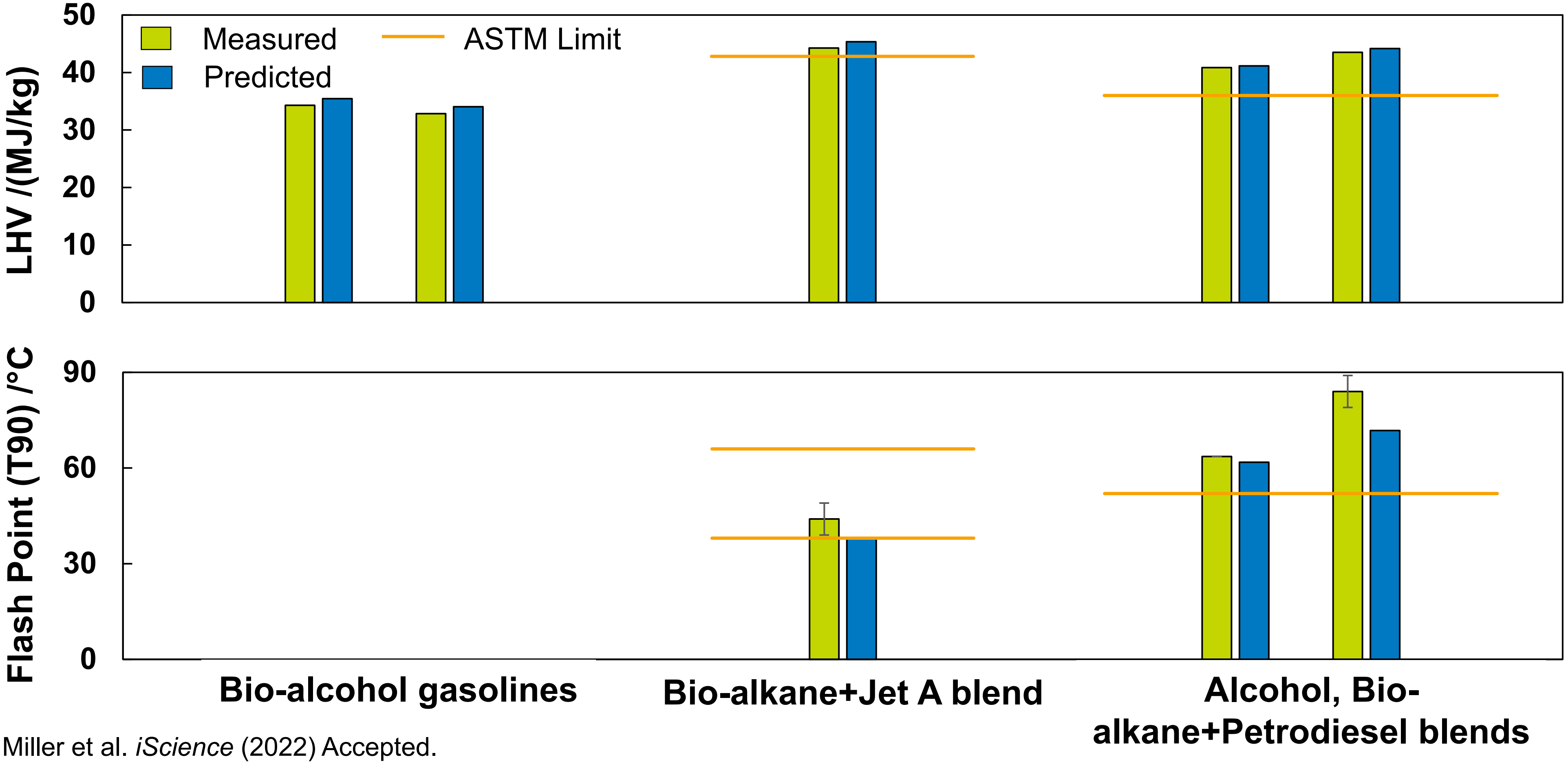




Miller et al. *iScience* (2022) Accepted.

Fuel property models *mostly* accurate

VULTURE-dictated fuel composition → Make surrogate mixture → Test major physical properties → Compare to model predictions



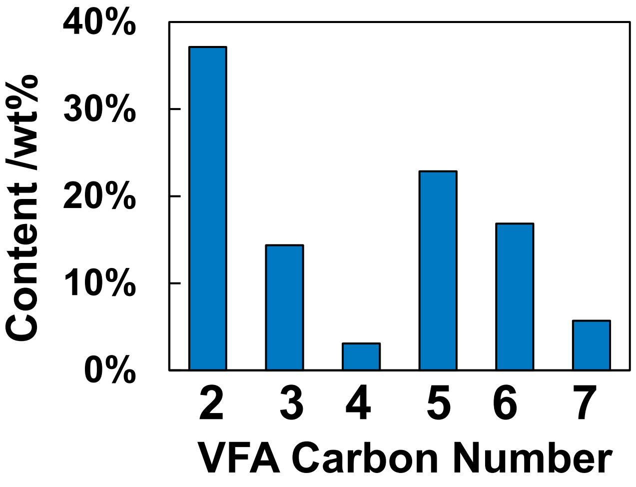
Lower heating value: Weighted average model accurate **within 2%!**

Flash point: Blending index models **underestimate** by 2-15°C.

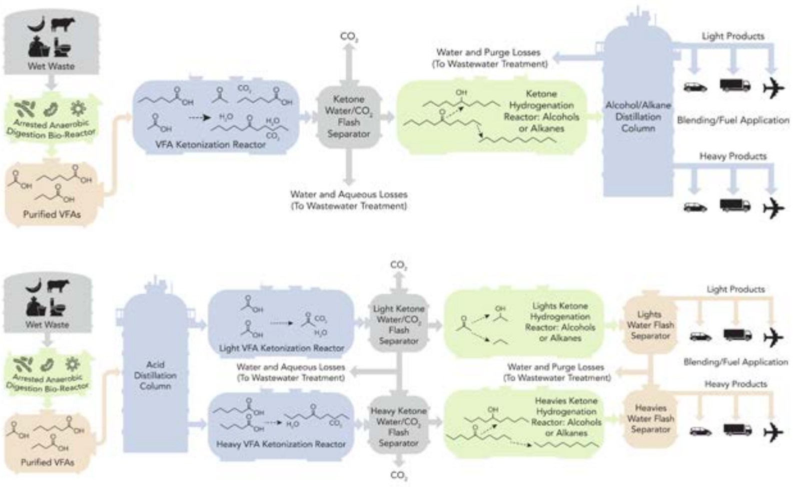
Miller et al. *iScience* (2022) Accepted.

Value of VULTURE: Rapid screening capability

VFA Mixture



Two process configurations



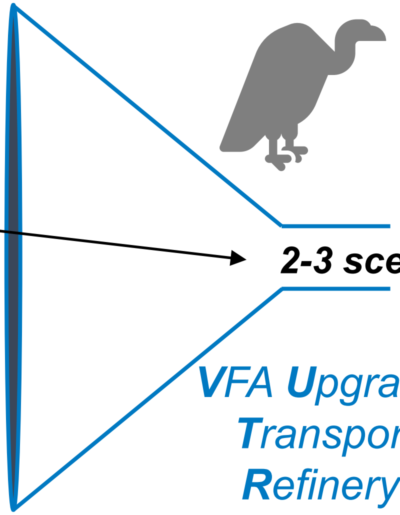
Process topology/ unit operation decisions

- Heavy/light key in distillations
- Hydrotreatment to alcohols or alkanes
- Final uses of each product stream (gasoline, diesel, jet)
- Determination of maximum blending level

480 scenarios!

Rigorous evaluation:
- Process simulation, TEA/LCA
- Surrogate synthesis, fuel property testing

*Not feasible for **all** scenarios*



2-3 scenarios

*VFA **U**pgrading to **L**iquid **T**ransportation f**U**els **R**efinery **E**stimation*

Rigorous evaluation:
- Process simulation, TEA/LCA
- Surrogate synthesis, fuel property testing

*Feasible for **a subset** of pre-selected promising scenarios*

Acknowledgements

- TEA: Matthew Wiatrowski, Avantika Singh
- LCA: Pahola T. Benavides, Troy Hawkins, Uising Lee, Yimin Zhang
- Slaughterhouse wastes anaerobic digestion: Eric Karp, Violeta Sànchez i Nogué, Stefan Haugen, Colin Kneucker
- Surrogate mixtures, fuel properties: Stephen Tifft, Earl Christensen, Teresa Alleman, Cameron Hays, Gina Fioroni, Jon Luecke
- Ideation: Derek Vardon, Nabila Huq, Stephen Tifft, Hannah Nguyen

Co-Optima Consortium

Better Fuels.
Better Engines.
Sooner.

NREL Transforming ENERGY 45Th anniversary

Argonne NATIONAL LABORATORY

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NREL/PR-5100-84538

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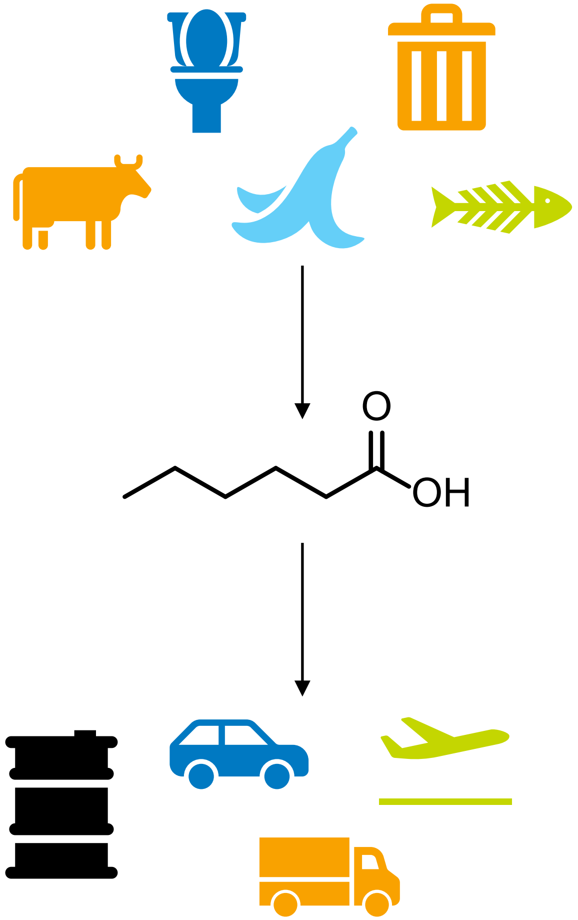

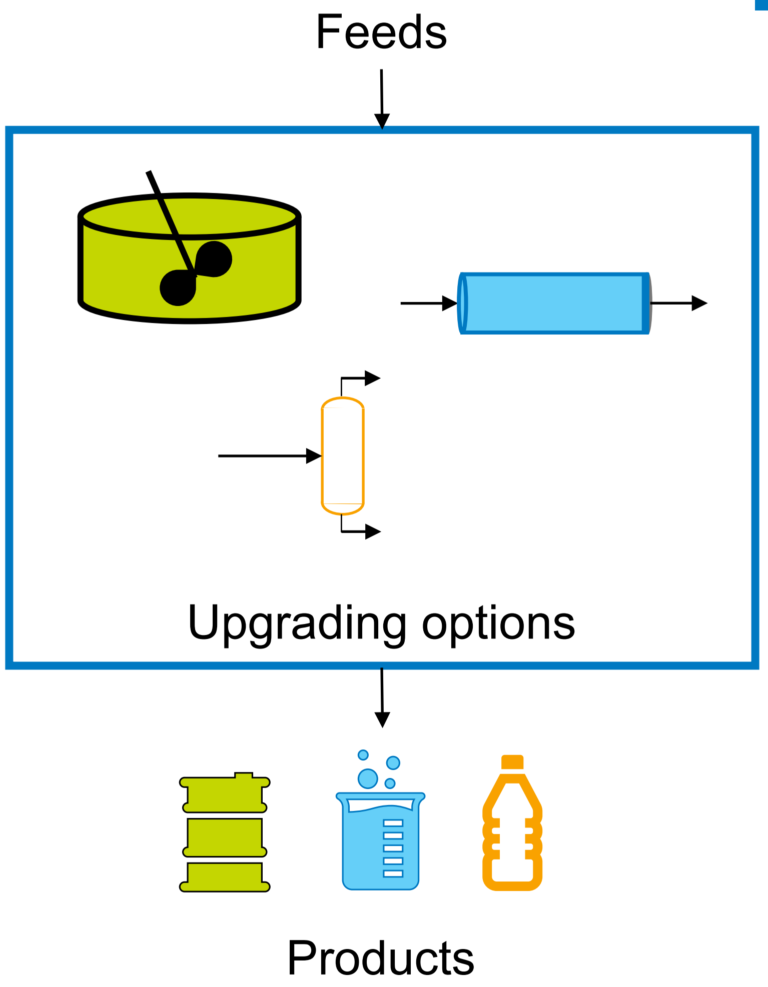

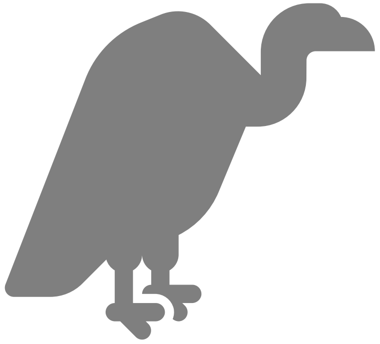

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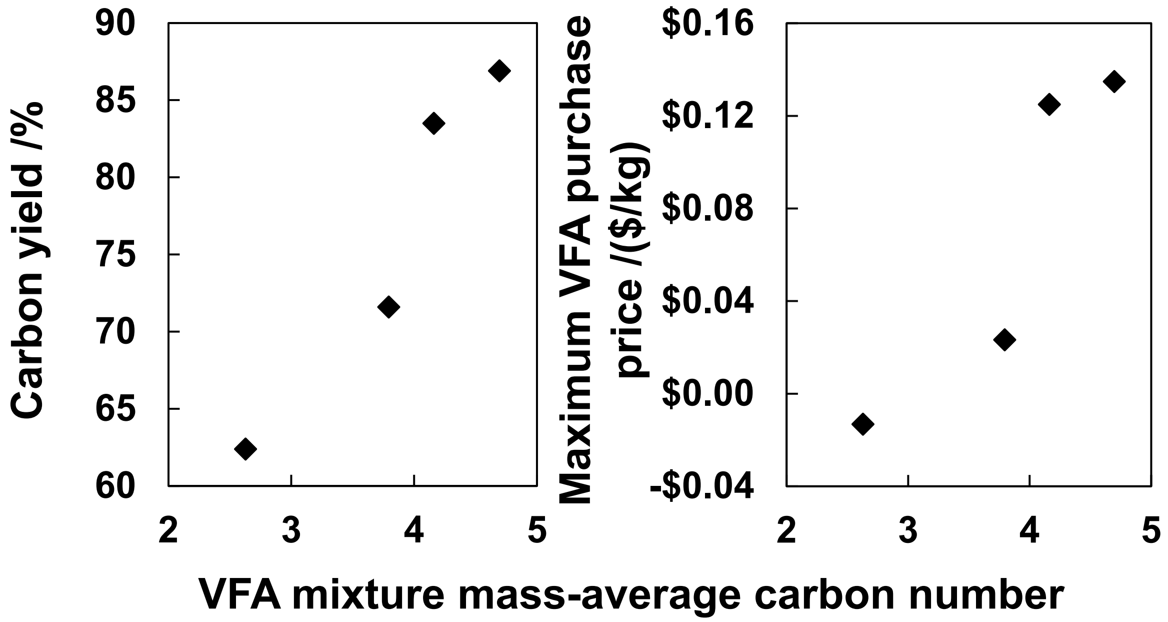
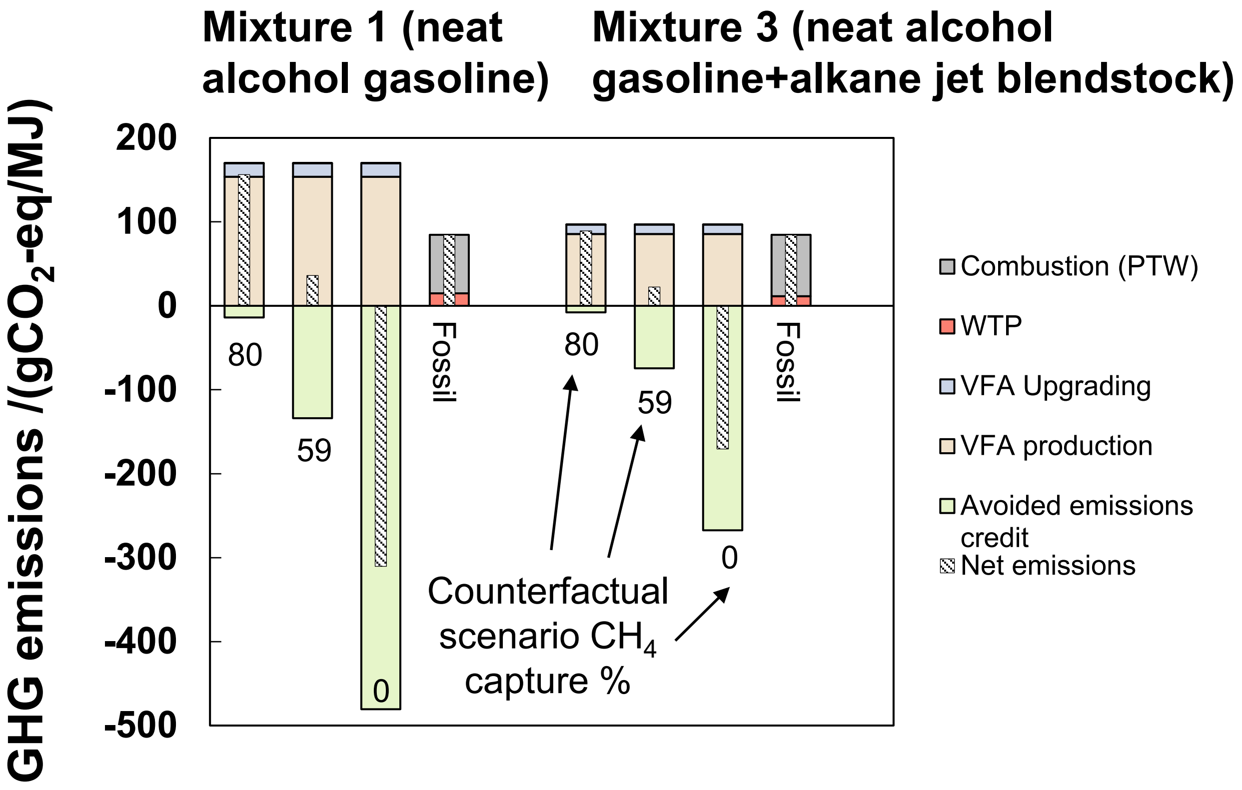
Promising economics, greenhouse gas emissions

Process technoeconomic analysis

- Plant size: 250 wet tons food waste/day (dictated by regional availability)
- Discounted cash flow rate of return analysis (assuming 10% internal rate of return)



Higher MW VFAs→Higher C yields, profitability



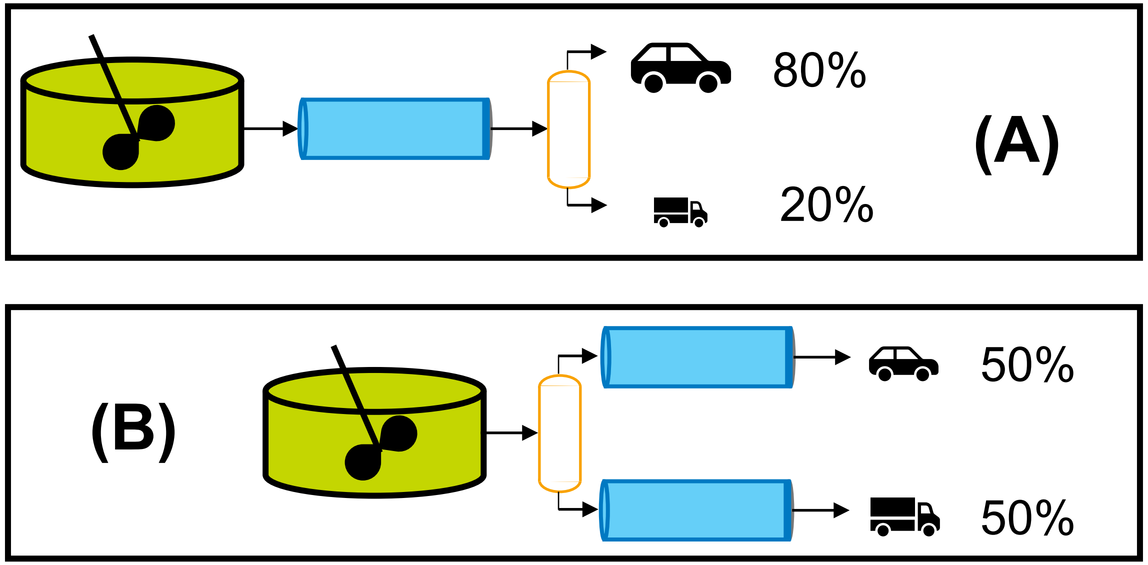
- 80% counterfactual CH_4 capture (~wastewater treatment)
- 59% counterfactual CH_4 capture (~landfill)
- 0% counterfactual CH_4 capture (~manure lagoon)

Potential for >50% GHG reduction or net negative emissions if utilizing feedstock with current insufficient CH_4 capture

Miller et al. *iScience* (2022) Accepted.

Even “simple” processes yield many operating choices

Process topology?



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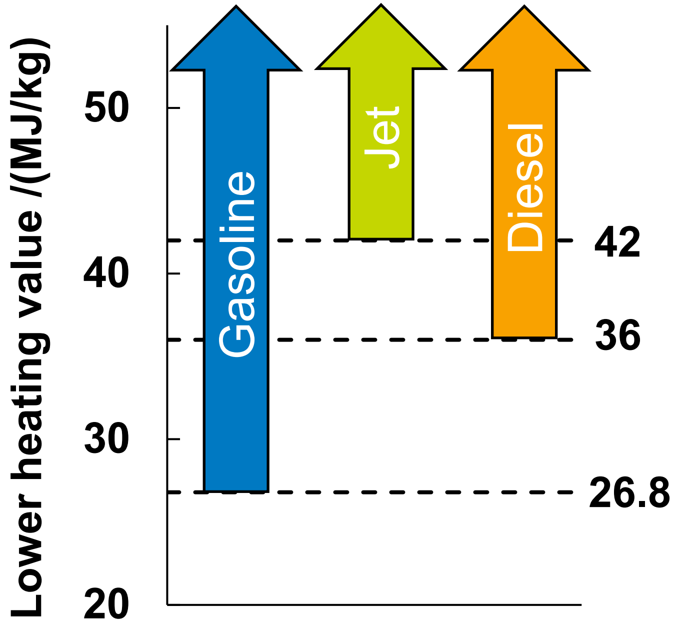
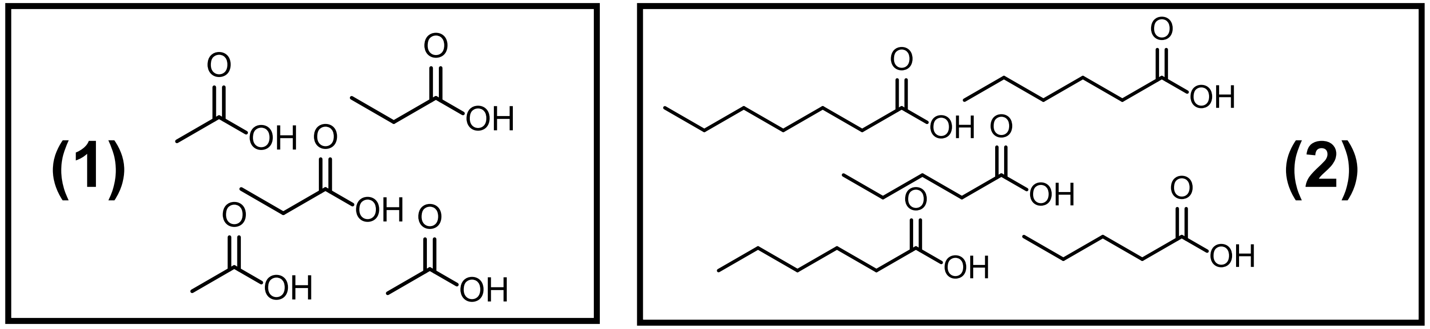
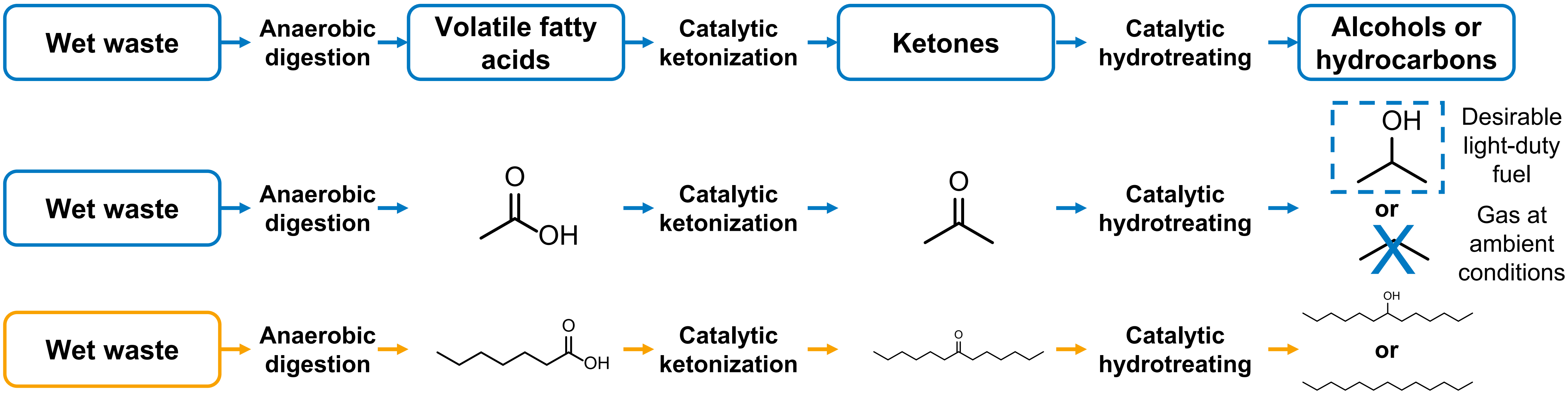


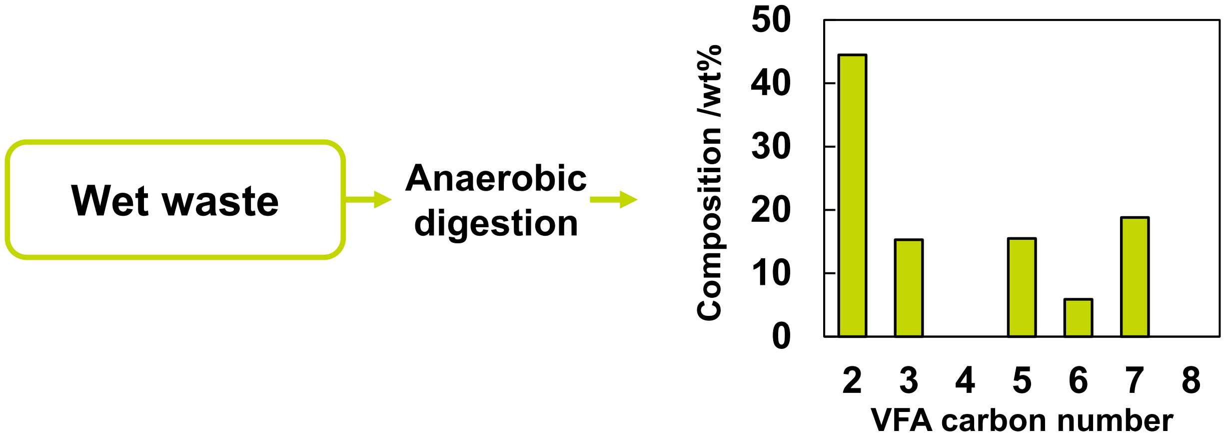
Feed stream contents?



Some decisions easy, most difficult



Alcohol-Diesel?
Alkane-Diesel? Jet?
No easy answer.



Not all VFAs necessitate the same unit operations.
Not all upgraded alcohols/hydrocarbons are best suited for the same applications.
Need: systematically decide what is "best."

Objective function defines goals

What might we want to optimize?

- High profit
- High fuel yield
- Low greenhouse gas emissions

We choose biocontent (BC):

$$BC = w_1 b_1 + (1 - w_1) b_2$$

- w_1: Weight fraction of upgraded product to fuel application 1
- $b_{1,2}$: Weight fraction of fuels 1,2 that is bio-derived

VFA mixture

Option 1

100% of fuel (w_1=1)→Diesel, blendable at 10% (b_1=0.1)

$$BC = 1 * 0.1 = \mathbf{0.1}$$

X

Option 2

20% of fuel (w_1=0.2)→Gasoline, neat (b_1=1); 80% of fuel→Diesel; blendable at 20% (b_2=0.2)

$$BC = 0.2 * 1 + 0.8 * 0.2 = \mathbf{0.36}$$

✓