Screening and evaluation of biomass upgrading strategies for sustainable transportation fuel production with biomass-derived volatile fatty acids

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Highlights
High-throughput screening for biomass upgrading process design
Applied to wet waste-derived volatile fatty acid upgrading to transportation fuels
Model assumptions compared to process simulation, fuel property testing results
Optimal upgrading strategy depends on the chain length of input acids

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SUMMARY

Biomass conversion to fuels and chemicals is crucial to decarbonization, but choosing an advantageous upgrading pathway out of many options is challenging. Rigorously evaluating all candidate pathways (process simulation, product property testing) requires a prohibitive amount of research effort; even simple upgrading schemes have hundreds of possible permutations. We present a method enabling high-throughput screening by approximating upgrading unit operations and drop-in compatibility of products (e.g., fuel properties) and apply it to volatile fatty acid (VFA) conversion to liquid transportation fuels via a MATLAB script, VFA Upgrading to Liquid Transportation fUels Refinery Estimation (VULTURE). VULTURE selects upgrading configurations that maximize fuel blend bio-derived content. We validate VULTURE’s approximations through surrogate fuel property testing and process simulation. Techno-economic and life cycle analyses suggest that VFA upgrading processes down-selected by VULTURE are profitable and have low carbon intensities, demonstrating the potential for the strategy to accelerate process development timelines at decreased costs.

INTRODUCTION

The mounting climate and environmental hazards resulting from over-utilization of fossil fuel resources for energy and materials compel the development of analogous processes which valorize renewable resources and proffer low (<30% of fossil fuels) or negative carbon intensities. Upgrading of biomass, which is projected to be available in the United States at $60 or less per ton in quantities greater than one billion tons per year by 2040, holds promise to replace fossil-derived resources for many applications. Processes for transforming biomass into useful fuels and chemicals, such as upgrading of syngas over metal and acid catalysts, and hydrotreatment of pyrolysis oil over supported metal catalysts or metal-doped zeolites, and upgrading of organic wet wastes to hydrocarbons via anaerobic digestion, catalytic ketonization, and hydrotreatment, often form heterogeneous product streams. These product streams are often best suited to be divided between multiple applications such as transportation fuels (e.g., gasoline, jet, or diesel) or commodity chemical precursors (e.g., olefins and aromatics). The composition of final products made by each of these processes can be altered by changing catalysts, catalytic upgrading conditions, separations parameters, or unit operation configurations. In this way, it is possible to tune the final products of biomass upgrading to desired sets of molecules.

Identifying desired sets of products is a non-trivial task that necessitates the definition of an objective function to be optimized, such as overall carbon yield, production of a certain molecule class, process profitability, or carbon intensity. Furthermore, the use of bioblendstocks is constrained by material property limits in applications such as transportation fuels, understanding blending limits for upgraded molecules with petrofuels also influences optimal upgrading configurations. Consideration of blending limitations of upgraded molecules, especially in fuels, is thus crucial to assessing the suitability of various upgrading scenarios and end uses. A thorough analysis of upgrading scenario choices entails the enumeration and evaluation of (i) all biomass or organic waste upgrading process options and (ii) all possible final...
products. This process would entail conducting rigorous process modeling, product surrogate synthesis and property testing, and techno-economic and life cycle analyses for every possible scenario. Such analysis is impractical for systems with many process parameter choices, in which hundreds of upgrading choices are possible for a given bioblendstock. A method of approximating each of these analyses would allow for the initial screening of all possible scenarios and facilitate the consideration of both (i) multiple catalytic upgrading operating choices and (ii) suitability of products of each candidate route for multiple end applications, enabling the selection of a smaller subset of upgrading scenarios for more rigorous evaluation.

We present in this work a methodology for accomplishing such high-throughput scenario screening by predicting (i) products formed via catalytic upgrading and (ii) properties of upgraded and blended products formed to aid the identification of a handful of favorable combinations of conversion processes and applications from hundreds of choices (Figure 1). This methodology is applied to upgrading of volatile fatty acids (VFAs), C$_2$-7 carboxylic acids formed from the bioprocessing of wet waste, an inexpensive biomass resource produced in the United States at enough volume to displace 20% of aviation fuel use. Upgrading of VFAs generally comprises catalytic ketonization followed by the catalytic hydrogenation of ketones to alcohols or alkanes; each of these steps has been demonstrated with close to 100% yield at the lab scale, demonstrating pathway viability. Conversion of wet waste-derived VFAs to fuels also avoids methane emissions which would otherwise result from traditional waste management options such as landfilling of organic wet wastes, giving these processes low to negative life cycle carbon emissions; this is crucial as methane is more than 20 times as efficient at trapping atmospheric heat as CO$_2$. Alcohols and alkanes formed by these upgrading processes are promising blendstocks for end fuel uses including gasoline, jet, or diesel. We approximate upgrading processes and blending capacity of upgraded molecules in petrofuels using a MATLAB script, the VFA Upgrading to Liquid Transportation Fuels Refinery Estimation (VULTURE), written for this work. We highlight that the VULTURE approach, applied here for VFA-derived fuels, is also translatable for other applications (e.g., commodity chemicals), mixtures of multiple application categories, and other feedstocks.

We rigorously analyze several promising scenarios identified by VULTURE using detailed process simulation, surrogate fuel property testing, and techno-economic and life cycle analysis to assess the validity of VULTURE’s approximations. Results of these validation exercises illustrate the accuracy and limitations of VULTURE’s upgrading assumptions, the comparative economic viability of VFA mixtures with varying
carbon chain lengths, and the decrease in life cycle carbon emissions associated with displacing petrofuels with VFA-derived transportation fuels. VULTURE’s assumptions are shown to be particularly robust for upgrading streams containing high concentrations of heavy (C₆-7) VFAs; losses of bio-carbon in upgrading of light (C₂-3) VFAs unanticipated by VULTURE result in comparatively lower economic viability for upgrading of feedstocks consisting of mostly light VFAs. We also show that upgrading feedstocks containing high concentrations of heavy (C₆-7) VFAs maximize yields of heavy-duty (diesel or jet) fuels. These results show that the strategy employed in VULTURE facilitates efficient, high-throughput screening of biomass upgrading pathways and products for advantageous upgrading configurations.

RESULTS

Volatile fatty acid upgrading unit operations and configurations

We model upgrading of VFA feedstocks to alcohols or alkanes using one of the two sequences of catalytic reaction and separations units shown in Figures 2 and S1. In upgrading configuration #1 (visualized in Figure 2), VFAs of varied chain length obtained via arrested anaerobic digestion of organic wet wastes (vide infra) are fed to a packed-bed vapor-phase ketonization reactor filled with a ZrO₂ catalyst. The reactor achieves 100% yield of ketones from VFAs; this result has been demonstrated on the laboratory scale with mixes of biogenically derived VFAs, 2 acetic acid, 3 and propionic acid. 23,33 Chain length distribution of ketones is predicted by the VFA coupling model utilized in our previous work (Note S1).2 Ketonization reactor effluent is fed to a flash separator which removes water and CO₂, stoichiometric ketonization co-products, from the ketone stream. The purified ketone stream then reacts with co-fed hydrogen to form alkanes or alcohols in catalytic packed-bed reactors; yields of both steps are assumed to be 100%. Ketone hydrodeoxygenation (HDO) to alkanes has been demonstrated at roughly theoretical yield in flow reactors using Pt/Al₂O₃ catalysts, 2,15 while Vardon et al. 26 and Zhu et al. 34 achieved near or equal to 100% yields of alcohols from central ketones over Pt-Sn alloys supported on activated carbon or similar catalysts, showing the feasibility of these pathways. After an intermediate flash separation of alkane or alcohol products from HDO co-product water and unreacted H₂, the final products are then separated into light and heavy streams for blending or neat use in fuel applications. The STAR methods section contains a more detailed explanation of flows, sizes, and operating conditions of all processing units.

We also considered a variation to upgrading configuration #1 in which VFAs were initially separated into light and heavy streams represented in upgrading configuration #2 (Figure S1). Both VFA streams are then upgraded in parallel ketonization and hydrotreating reactors accompanied by associated separation units. Process and economic implications of the difference between upgrading configurations #1 and #2 are discussed later in discussion.

Fuel properties and specification limits

Optimal utilization of VFAs is determined by the potential to blend upgraded molecules into petrofuels or use them as neat fuels. The suitability of upgraded alcohols and alkanes for blending depends, in turn, on the fuel properties of individual upgraded bioblendstock components, properties of fuel mixtures, and application-specific limitations on fuel properties that ensure engine safety and operability. We identified seven fuel properties: boiling point (T₉₀, BP), flash point (FP), energy density (lower heating...
value, LHV), viscosity (at 40°C for diesel, 100°C for jet, and 25°C for gasoline; μ), melting point (cloud point for diesel, MP), water solubility (WS), and ignition quality (cetane number (CN) for diesel and jet; research octane number (RON) for gasoline), as broadly important for diesel, jet, and gasoline applications and gauged operability of fuels based on conformance to limits on these properties. Individual component molecular fuel properties are listed in our GitHub repository (Note S2), while the mixture property calculation formulas are shown in Table S1. Property limits for diesel, jet, and gasoline fuels as well as corresponding properties of pure petrofuels are listed in Table 1.

We acknowledge that the fuel properties evaluated by VULTURE do not encompass every ASTM specification for each fuel application, such as required jet engine seal swell characteristics, but they provide a reasonable set of first approximations which identify promising fuel mixtures. Mixtures which do not meet the specifications used in this work are likely not suitable for further study or advanced ASTM testing and thus do not merit further consideration.

VULTURE simulates upgrading, cutting, and blending of volatile fatty acid mixtures

We developed the VULTURE MATLAB script (see Note S2), which rapidly (in ~1 min) simulates all possible combinations of the catalytic upgrading and separations procedures for an input VFA mixture (upgrading configuration, choice of distillation light and heavy keys, production of alcohols or ketones, and target fuel application) outlined in the first section of the Results. Since most variables in the MATLAB model are discrete (i.e., non-continuous) and many of the limiting variables (e.g., flash point) are highly non-linear, we do not compactly express the model outside of the MATLAB code. Each scenario output by VULTURE simulates the creation of pairs or single fuels and/or fuel blends that satisfy the property limitations for drop-in usage explicated in the preceding section. This is enabled by an algorithm built into VULTURE which simulates (i) cutting VFAs and upgraded molecules into all possible pairs of light and heavy fractions and (ii) finding the maximum blending capacity into all possible petrofuels (gasoline, jet, and diesel) of each upgraded mixture before a critical fuel property specification is violated. After VULTURE enumerates all possible upgrading scenarios which create specification-compliant fuels or fuel blends, outputs were analyzed to identify scenarios that create pairs of (or single) fuels and fuel blends that maximize biocontent (BC, Equation 1):

$$ BC = w_1b_1 + (1 - w_1)b_2 $$ (Equation 1)

Equation 1 depends upon the weight fraction of the initial bioblendstock routed to fuel 1 ($w_1$) and the bio-derived content (weight fraction) of each fuel in the pair ($b_1$ and $b_2$). Note S3 and Figure S2 contain a thorough explanation of this algorithm along with an illustrative example of it in practice.

Case studies: Optimal utilization of various VFA distributions

The high-throughput simulation strategy enabled by VULTURE allowed us to rapidly identify promising upgrading strategies for upgrading of five different VFA mixtures obtained from the anaerobic digestion of slaughterhouse wastes (Figure 3, first column). Distributions 1—4 came from separate experiments, while distribution 5 is a blend of equal proportions of distributions 1—4. VFA distributions 1 and 2 comprise primarily light (C$_{2-3}$) VFAs, distributions 3 and 4 contain mostly heavier (C$_{5-6}$) VFAs, while distribution 5 contains roughly equivalent amounts of light and heavy VFAs.

### Table 1. Physical property specification limits for diesel, jet, and gasoline and neat petrofuel physical properties

| Fuel          | BP/T90/°C | FP/°C | LHV/(MJ/kg) | μ/cP  | MP/°C | WS/(g/L) | CN/RON |
|---------------|-----------|-------|-------------|-------|-------|----------|--------|
| Diesel-Lower  | –         | 52    | 36          | 1.615 | 40    | –        | 40 (CN) |
| Diesel-Upper  | 338       | –     | –           | 3.485 | –     | 0        | 2      |
| Diesel-Neat   | 335       | 61    | 42.6        | 2.663 | 40    | –9.7     | 46.8 (CN) |
| Jet-Lower     | –         | 38    | 42          | –     | –     | –        | 45 (CN) |
| Jet-Upper     | 300       | –     | –           | 10.08 | –     | –40      | –      |
| Jet-Neat      | 271       | 48    | 43.01       | 7.66  | –     | –52      | 48.4 (CN) |
| Gasoline-Lower| –         | –     | 26.8        | –     | –     | –        | 87.5 (RON) |
| Gasoline-Upper| 171       | –     | –           | –     | –     | –        | –      |
| Gasoline-Neat | 171       | –     | 42.83       | –     | –     | –        | 87.5 (RON) |

Note: Neat petrofuels are clay-treated diesel, Jet A, and RBOB gasoline. Property abbreviations are spelled out fully in Table S1 and in the text.
Figure 3. VULTURE results: Maximizing four objective functions in upgrading five VFA mixtures to transportation fuels

Mass-averaged carbon number, $<N_c>$, is listed for each mixture (see Equation 3 later in discussion). Objective functions are: (1) maximum bioblendstock content, alcohols only, (2) maximum bioblendstock content, alcohols or alkanes, (3) maximum bioblendstock utilization toward alcohol diesel, and (4) maximum bioblendstock utilization toward alcohol or alkanne heavy-duty fuels (diesel or jet). Fuel product table entries are highlighted according to their type (gasoline: lime green, jet: blue, and diesel: orange). Surrogates of fuel mixtures marked with asterisks were blended for fuel property testing (results in Figure 4), and upgrading scenarios typed in bold were validated using rigorous process simulation (Figures 5 and 6). Bio-content (wt %) of each fuel blend is listed in parentheses following each fuel unless listed as “neat” ($b_1$ and $b_2$, Equation 1). Weight fraction of bioblendstock routed to each fuel ($w_1$ and $w_2$, Equation 1) is listed at the bottom right corner of each table entry and cumulative bio-content of each sub-scenario is also listed in unshaded cells below each pair of fuels. Further details corresponding to each scenario are listed in Table S3. ROH denotes alcohols and HC denotes hydrocarbons.

| VFA mixture | 1) ROH, max biocontent | 2) ROH+HC, max biocontent | 3) ROH, max HD biocontent | 4) ROH+HC, max HD biocontent |
|-------------|------------------------|---------------------------|---------------------------|-----------------------------|
| $<N_c>$=3.8 | $C_{11.13}$ alcohol diesel blend (40%) $w_1=93%$ | $C_{11.13}$ alcohol diesel blend (40%) $w_1=93%$ | $C_{6.13}$ alcohol jet blend (82%) $w_1=98%$ | $C_{6.13}$ alkane jet blend (82%) $w_1=98%$ |
|             | Neat $C_3$ alcohol gasoline* | Neat $C_3$ alcohol gasoline* | Neat $C_3$ alcohol gasoline* | Neat $C_3$ alcohol gasoline* |
|             | Configuration 1; 94% bio-content | Configuration 1; 94% bio-content | Configuration 1; 99% bio-content | Configuration 1; 99% bio-content |

| VFA mixture | 4) ROH+HC, max HD biocontent |
|-------------|-----------------------------|
| $<N_c>$=7.1 | $C_{6.13}$ alkane jet blend (82%) $w_1=93%$ |
|             | Neat $C_3$ alcohol gasoline* |
|             | Configuration 2; 93% bio-content |

| VFA mixture | 1) ROH, max biocontent | 2) ROH+HC, max biocontent |
|-------------|------------------------|---------------------------|
| $<N_c>$=1.0 | $C_{2.13}$ alcohol diesel blend (39%) $w_1=66%$ |
|             | Neat $C_3$ alcohol gasoline* |
|             | Configuration 1; 75% bio-content |

| VFA mixture | 1) ROH, max biocontent |
|-------------|------------------------|
| $<N_c>$=2.6 | Neat $C_3$ alcohol gasoline* |
|             | Configuration 1; 60% bio-content |

| VFA mixture | 1) ROH, max biocontent |
|-------------|------------------------|
| $<N_c>$=2.6 | Neat $C_3$ alcohol gasoline* |
|             | Configuration 1; 60% bio-content |
The optimality of VFA upgrading scenarios was quantitatively evaluated using four different objective functions, which are listed in the top row of Figure 3. Sub-scenarios satisfying objective function 1 (alcohols (ROH) only, maximize BC) maximize the value of Equation 1 (total BC) for a given VFA distribution using pairs of fuels made up of alcohols only (diesel and gasoline; alcohols cannot be used as jet fuels). Similarly, objective function 2 also seeks to maximize total BC using pairs of alcohol or alkane fuels (ROH + HC). Objective functions 3 and 4 are similar to 1 and 2 in that 3 considers alcohol-only scenarios and 4 considers alcohol or alkane fuels, but these two objective functions maximize the bio-content of only heavy-duty (diesel or jet) fuels ($BC_{HD}$), represented numerically as a truncated variation of Equation 1:

$$BC_{HD} = w_{HD} b_{HD}$$

(Equation 2)

In Equation 2, $w_{HD}$ is the weight fraction of bioblendstock utilized in heavy-duty fuel and $b_{HD}$ is the bio-content (weight fraction) of the heavy-duty fuel. Figure 3 lists fuel contents, upgrading configurations, and total bio-content of sub-scenarios that satisfy each objective function for each VFA distribution. Predicted properties of fuels created in each of these sub-scenarios, as well as the sub-scenario with maximum alkane diesel utilization (Sub-scenario 2.Extra), are listed in Table S3. Sub-scenarios are indexed by their VFA distribution and the satisfied objective function (e.g., the first row of Figure 3 contains Sub-scenarios 1.1–1.4).

The results presented in Figure 3 and Table S3 show that the content of VFA feedstocks greatly influences the identity of optimized upgraded fuels. Feedstocks consisting of mostly light VFAs are most optimally upgraded in scenarios that maximize the production of gasoline-applicable alcohols. For example, VFA distribution 1, which contains exclusively C5 and lower VFAs (C2–C4 95 wt % C2-3) can be utilized entirely as neat gasoline (Sub-scenarios 1.1 and 1.2), although heavy components can be separated to yield diesel (1.3) or jet (1.4) blends. Even in these cases, however, only 10–15 wt % of the bioblendstock is routed to heavy-duty fuel applications and overall BC is lowered (88 and 95%) compared to Sub-scenarios 1.1/1.2 (100%).

In contrast, VULTURE shows that heavier VFA mixtures such as distributions 3 and 4 (mass-averaged VFA carbon number, $\langle N_C \rangle ≥ 4.7$) are best upgraded in with processes that route substantial amounts of upgraded compounds to heavy-duty fuels. A majority ($w_1 ≥ 77$ wt %) of VFAs go toward the production of jet or diesel fuel blends in all eight sub-scenarios for upgrading VFA distributions 3 and 4, while light products are converted to neat alcohol gasoline. Sub-scenarios 3.2 and 3.4 (identical) displace petrofuels the second-most efficiently of all scenarios (99 wt % total bio-content) and also feature the highest heavy-duty fuel bio-content (76 wt %) of all sub-scenarios (Figure 3, Table S3).

Broader examination of the optimized fuel pairs presented in Figure 3 and Table S3 gives rise to several conclusions:

1) VULTURE successfully narrows considered upgrading options by roughly two orders of magnitude for a given bioblendstock. For example, Table S2 shows that only five scenarios for upgrading VFA mixture 5 (two pairs of which are identical) out of 430 possibilities (80 of which are valid, see Note S3) achieve total bio-content above 50%.

2) Sub-scenarios producing pairs of fuels (all besides 1.1 and 1.2) always yield one light- and one heavy-duty fuel. This is not specified by VULTURE, but light ($C_{3-7}$) molecules are best utilized as gasoline and heavy ($C_{5-13}$) molecules are best utilized as diesel or jet fuel.

3) Upgrading configurations 1 and 2 are both useful in different situations. Out of the 18 sub-scenarios presented in Figure 3 that form pairs of fuel products, nine use upgrading configuration 1, while the other nine use configuration 2. Significantly, all seven sub-scenarios which produce aviation fuel utilize upgrading configuration 2; this indicates that the necessity of producing high quantities of C9 alkanes for jet fuel is best accomplished with configuration 2’s approach of separating VFAs into light and heavy ($C_{4-5}$) fractions and ketonizing each separately, creating two distinct groups of products by carbon number (e.g., C3,7 and C9,13 in Sub-scenario 3.2). This constraint does not exist for alcohol diesel fuel scenarios, as nine out of eleven of these utilize upgrading configuration 1 and form one continuous distribution of products by carbon number (e.g., C3,13 in Sub-scenario 5.1, see Figure S2A), while the other two sub-scenarios use configuration 2.

4) The carbon number range of fuels made from the VFA profiles considered here is better-adapted to generating high-bio-content alkane aviation fuel blends than diesel blends even though either alkanes or alcohols can be utilized in diesel fuel. This trend arises in comparison of pairs of
Figure 4. Measured and predicted fuel properties of VULTURE-generated liquid transportation fuels
(A–G) shows boiling point (T90), (B) shows flash point (error bars correspond to uncertainty in the analytical measurement), (C) shows lower heating value (LHV), (D) shows dynamic viscosity, (E) shows melting point (cloud point for diesel), (F) shows water solubility, and (G) shows research octane number (RON, gasoline) or cetane number (CN, jet, and diesel). If fuel specification limits are not paired, arrows indicate if limits are upper (down arrow) or lower (up arrow). * Lower limit of
VULTURE accurately predicts most mixture fuel properties

We created surrogate mixtures of five fuels and fuel blends recommended by VULTURE; four of these mixtures are indicated by asterisks in Figure 3. Additional details about the contents of these four mixtures and the fifth (Scenario 2.Extra) are described in the experimental procedures and Tables S3 and S4. VULTURE-predicted and measured boiling point (T90, Figure 4A), flash point (4B), lower heating value (LHV, 4C), dynamic viscosity (4D), melting point (4E), water solubility (4F), and RON (gasoline) or CN (jet and diesel; 4G) of all evaluated fuels are displayed in Figure 4. This figure shows that VULTURE’s model equations are broadly accurate at predicting drop-in-relevant properties of fuel mixtures and ensuring that the mixtures adhere to ASTM specification limits for targeted transportation fuel applications (Table 1). VULTURE does consistently underpredict boiling point/T90 values (Figure 4A) and overpredict water solubilities of light alcohol gasolines (Figure 4F), but these inaccuracies do not cause properties of any VULTURE fuels to fall dramatically far from specification limits. Veracity of viscosity and flash point predictions is particularly significant, as properties of these mixtures are not approximated well as linear combinations of individual component properties. We discuss the accuracy of VULTURE’s predictions in greater detail in Note S4.

Detailed process simulation shows the accuracy of most VULTURE assumptions

We compared carbon flows through VFA upgrading units assumed by VULTURE to those generated by an Aspen Plus simulation to analyze the accuracy of the assumptions. Upgrading facility models with an input of 1100 kg h⁻¹ VFAs were formulated for four sub-scenarios: 2.Extra, 3.2, 1.1, and 5.1 (Figures 5 and S5). These scenarios model production of all fuel types considered in this work, including an alkane diesel blendstock (2.Extra), an alkane jet blendstock (3.2), an alcohol diesel blendstock (5.1), and alcohol gasoline (all scenarios). VULTURE incorporates carbon losses to ketonization co-product CO₂ and thus predicts carbon efficiencies (quotient of effluent fuel carbon flows and influent VFA carbon flows) between 78.8 and 87.4% for all scenarios (Figures 5 and S5). Detailed Aspen Plus modeling highlights two phenomena not anticipated by VULTURE, aqueous losses and purge losses, that result in carbon yield decreases. Aqueous carbon losses occur due to the solubility of light ketones in co-product water (40–50% acetone losses, <20% 2-butanone losses, <10% C₅+ ketone losses). These aqueous losses exit the process in the post-ketonization separations unit (Figures 2 and S1) and are routed to wastewater treatment. Purge losses reflect the entrainment of alcohols and hydrocarbon jet fuel. We examine the fidelity of fuel properties and unit operation performance predicted by VULTURE in the following sections.

Figure 4. Continued

melting point measurement is –70°C; fuel melts below this temperature. ** Lower detection limit of water solubility test is 100 mg/L; no fuel was detected. Water solubilities of jet and diesel are multiplied by 10 (x10) for visual clarity. Gasoline 1: Alcohols, Sub-scenario 1.1; Gasoline 2: Alcohols, Sub-scenario 3.1; Jet: Alkane and Jet A blend, Sub-scenario 3.1; Diesel 1: Alcohol and fossil diesel blend, Sub-scenario 5.1; Diesel 2: Alkane and fossil diesel blend, Sub-scenario 2.Extra.
hydrocarbons in the recycled H₂ stream exiting the hydrogenation reactors (Figures 2 and S1); these losses are minor (<0.3%) and do not significantly impact process carbon efficiency.

Figures 5 and S5 show that the incorporation of these two phenomena not captured by VULTURE, especially aqueous losses, significantly decreases process carbon efficiency. The carbon efficiencies of two sub-scenarios, 1.1 and 2.Extra, drop by greater than 10% (16.4 and 12.3%, respectively), mostly due to aqueous losses. Notably, carbon efficiencies of the other two sub-scenarios, 3.2 and 5.1, drop much less dramatically (0.5 and 3.1%, respectively) when incorporating these non-idealities.

The carbon number distribution of fuels and fuel blends produced in each sub-scenario as modeled by VULTURE and Aspen Plus is shown in Figures 6 (2.Extra and 3.2) and S6 (1.1 and 5.1). The contents of light gasolines in all four scenarios vary appreciably between VULTURE and Aspen Plus predictions resulting from the aqueous light ketone losses unanticipated by VULTURE. The content of light ketones in each gasoline is overpredicted in VULTURE by between 2 (Sub-scenario 3.2) and 11 (Sub-scenario 2.Extra) wt %, while the C₅+ alcohol content is underpredicted in VULTURE by up to 5 wt % since aqueous losses of these molecules are minimal. Additionally, the gasoline-bound streams contain low (<2 wt %) concentrations of alcohols with higher than intended chain lengths (e.g., C₈–₉ alcohols in the intended C₃–₇ mixture in Sub-scenario 3.2) due to imperfect separations of VFAs or alcohols.

Figures 6 and S6 also show that detailed process modeling of heavy-duty fuel production predicts fuels with contents similar to VULTURE predictions, with less than a 6 wt % discrepancy in content for all fuels. Thus, VULTURE’s assumptions are quite robust when applied to processes forming heavy-duty alcohol and alkane transportation fuels. The Aspen Plus simulation also tracked the entrainment of water and permanent gases (H₂O, CO₂, and H₂) in liquid fuels and revealed that no fuel contained more than 0.81 wt % of these species combined, showing that VULTURE’s assumption that these species are not present in liquid fuels is also close to accurate. Figures 6 and S6 also illustrate that VULTURE’s assumption of the perfect separation between VFAs or ketones of different carbon numbers is close to accurate. The alcohol separations column used in Sub-scenario 5.1 (upgrading configuration #1) sends only negligible amounts (<0.3 wt %) of C₂–₆ and C₇–₁₃ alcohols to diesel and gasoline blendstocks, respectively.
Similarly, the VFA distillation columns employed in Sub-scenarios 2.Extra and 3.2 (upgrading configuration #2) produce VFA streams with low (~2 wt % or less) concentrations of VFAs intended for the other stream. The presence of low concentrations of these light VFAs in heavy streams also slightly alters the carbon distributions of final alkanes, with low amounts of C7-8 alkanes (1.3 wt %) and C11-12 alkanes (2.0 wt %) present in the C9-13 jet blendstock in Sub-scenario 3.2 (Figure 6A) and in C13 diesel blendstock in Sub-scenario 2.Extra (Figure 6B), respectively. Comparison of liquid fuel product contents predicted by VULTURE and rigorous process modeling (Aspen Plus captures non-idealities in separations such as azeotropes) shows that the separation assumptions made by VULTURE, while not perfect, give a viable first approximation of rigorously modeled process flows.

The trends in process carbon efficiency between VFA upgrading scenarios can also be viewed through the lens of mass-averaged carbon numbers ($<N_C>$) of each VFA input stream. This quantity is calculated from the weight fractions of each VFA in a distribution:

$$<N_C> = \sum_{i} w_i N_{C,i} \tag{Equation 3}$$

In Equation 3, $w_i$ is the mass fraction and $N_{C,i}$ is the carbon number of VFA $i$. The VFA distribution plots in Figure 3 indicate that this quantity varies among the VFA distributions used in modeling cases from 2.6 (Sub-scenario 1.1) to 4.7 (Sub-scenario 3.2). Figure S7A shows process carbon yields from both VULTURE and Aspen Plus models increase with increasing $<N_C>$. One contribution to this trend, captured in both models, is the loss of CO2 occurring with ketonization. The loss of one carbon as CO2 in self-ketonization of acetic acid results in a carbon yield to acetone of only 75%, whereas the loss of one carbon as CO2 in self-ketonization of heavier heptanoic acid results in a carbon yield to 7-tridecanone of 93%. Thus, upgrading larger VFAs (or VFA distributions with larger $<N_C>$) will intrinsically result in higher process carbon yields. The second major phenomenon contributing to losses of carbon yield is the solubility of short-chain ketones in the water produced from ketonization, as discussed above, resulting in process carbon losses to the post-ketonization aqueous phase. The Aspen Plus carbon yield plot in Figure S7A illustrates that these losses also decrease with increasing VFA distribution $<N_C>$. Thus, both aforementioned factors cause the carbon efficiency of VFA upgrading to increase as inlet VFA chain length increases. VULTURE qualitatively captures this trend, but Aspen Plus modeling shows that the trend is steeper than VULTURE predicts.

Figure 6. VULTURE-predicted and ASPEN Plus-modeled contents of VULTURE-generated transportation fuels delineated by carbon number. (A) depicts fuel contents from Sub-scenario 2.Extra and (B) depicts fuel contents from Sub-scenario 3.2. Contents of fuels from Sub-scenarios 1.1 and 5.1 are in Figure S6.
Techno-economic analysis: economic viability corresponds to volatile fatty acid chain length

Using the aforementioned process models developed in Aspen Plus, we performed a techno-economic analysis (TEA) on each of the four scenarios outlined in Figures 5 (and S5) and 6 (and S6) to demonstrate the economic prospects of VULTURE-generated upgrading schemes. The TEA considered a VFA upgrading facility using purified mixed VFAs as a feedstock for the production of various biofuels and used a discounted cash flow rate of return (DCFROR) analysis to quantify the maximum VFA purchase price allowable to ensure the economic viability of the upgrading facility given fixed fuel selling prices (Table S6). TEA results for each scenario are shown in Table 2. The maximum VFA purchase price ranged from $0.13/kg for Sub-scenario 3.2, indicating that this scenario would be economically viable if the mixed VFAs could be produced/acquired at a cost of $0.13/kg or less, to -$0.01/kg for Sub-scenario 1.1, indicating that this scenario would not be economically viable unless a net credit of $0.01/kg was associated with VFA production.

Figure S7B shows the maximum VFA purchase price as a function of $<N_c>$ of each VFA distribution in the four sub-scenarios used for detailed modeling. The maximum VFA purchases price increases monotonically with $<N_c>$, from -$0.01/kg to $0.13/kg as mass average carbon number increases from 2.6 to 4.7. This minimum purchase price increase with carbon number reflects that biorefineries with configurations described in this work are more economically viable when intaking influent feed rich in longer-chain (e.g., C₄+) VFAs, mirroring the correlation of $<N_c>$ with carbon yield to fuels (Figure S7A) and suggesting that carbon yield is the principal driver of process economics in VFA upgrading to liquid transportation fuels.

Table 2. Summary of techno-economic analysis of VFA upgrading scenarios generated by VULTURE

| Scenario | 1.1 (Single product) | 2. Extra (Configuration #2) | 3.2 (Configuration #2) | 5.1 (Configuration #1) |
|----------|----------------------|-----------------------------|------------------------|------------------------|
| Max VFA Purchase Price ($/kg) | -$0.01 | $0.02 | $0.13 | $0.12 |
| Max VFA Purchase Price ($/gal) | -$0.05 | $0.09 | $0.49 | $0.47 |
| $<N_c>$ | 2.6 | 3.8 | 4.7 | 4.1 |
| Primary fuel products | Gasoline-range alcohols | Gasoline-range alcohols & diesel-range hydrocarbons | Gasoline-range alcohols & SAF-range hydrocarbons | Gasoline-range alcohols & diesel-range alcohols |
| Total fuel yield (GGE/tonne VFA) | 117 | 151 | 210 | 187 |
| Gasoline | 117 | 103 | 42 | 55 |
| Diesel | 0 | 48 | 0 | 132 |
| Jet | 0 | 0 | 168 | 0 |
| Total fuel yield (MM GGE/yr) | 0.92 | 1.19 | 1.66 | 1.48 |
| Gasoline | 0.92 | 0.81 | 0.33 | 0.43 |
| Diesel | 0.00 | 0.38 | 0.00 | 1.05 |
| Jet | 0.00 | 0.00 | 1.33 | 0.00 |
| Fuel carbon yield | 62.4% | 71.6% | 86.9% | 83.5% |
| Gasoline | 62.4% | 48.8% | 17.4% | 24.5% |
| Diesel | 0.0% | 22.8% | 0.0% | 59.0% |
| Jet | 0.0% | 0.0% | 69.4% | 0.0% |
| Fixed Capital Investment ($MM) | 4.33 | 5.80 | 5.79 | 4.67 |
| Non-VFA Operating expenditures ($MM/yr) | 1.22 | 1.22 | 1.09 | 1.07 |
| Hydrogen | 0.21 | 0.20 | 0.26 | 0.21 |
| Catalysts | 0.11 | 0.09 | 0.06 | 0.11 |
| Utilities | 0.28 | 0.24 | 0.08 | 0.12 |
| Fixed costs | 0.62 | 0.69 | 0.69 | 0.63 |
The impact of carbon efficiency appeared to be stronger than any differences in capital or operating costs between cases. The fixed capital investment (FCI) for each facility ranged from $4.3-$5.8 MM and was higher for pathways with two parallel upgrading trains (Sub-scenarios 3.2 and 2.Extra, configuration #2; Figure S1). Despite this, Sub-scenario 3.2 had the most promising economics, suggesting that the added cost of the more complex upgrading train is justified. Similarly, Sub-scenario 1.1 had the lowest capital costs but also the lowest minimum VFA purchase price. Operating costs were lower for cases with higher fuel yields, despite increased hydrogen requirements; this can be attributed to the wastewater treatment costs incurred for cases with higher aqueous ketone losses. Thus, VFA profiles with lower \( \langle N_c \rangle \) incur an additional penalty of increased operating costs on top of lower carbon efficiencies, further highlighting the benefits of longer-chain VFA profiles.

The scale of the facility modeled here (250 wet tons of food waste/day, assumed to be limited in size by the regional availability of food waste from which the VFAs are derived) is much smaller than those typically considered for a biorefinery utilizing lignocellulosic feedstocks\(^{41,42}\) and may render the use of multiple catalytic upgrading trains impractical. Larger facility scales using a wider range of available feedstocks such as animal manure and wastewater sludge may be more practical applications for complex upgrading strategies.\(^{22}\) To make this economic analysis applicable to feedstocks at varying scales, a sensitivity analysis was also performed on each case to demonstrate how the maximum VFA purchase price changes at different facility sizes. Figure S8 shows that a significant economy of scale benefit is observed for all cases if the VFA precursors are abundant enough to support the specified VFA feed scales, with maximum VFA purchase prices of over $0.30/kg for the most promising scenario (Sub-scenario 3.2) being carried out at a plant with throughput of 200 ton/day. At this 200 ton/day scale, all analyzed scenarios have maximum VFA purchase prices above $0.17/kg, showing that VULTURE-generated scenarios have profitability potential.

**Carbon intensity of volatile fatty acid-derived fuels is substantially lower than petrofuels**

We used life cycle analysis (LCA) to evaluate greenhouse gas (GHG) emissions of the previously discussed VFA upgrading pathways. The total life cycle GHG emissions for the four pathways were compared to the life cycle emissions of the conventional petroleum counterpart of the heaviest-duty fuel produced in each scenario as shown in Table S5 and Figure 7. Emission reductions of the four VFA-derived pathways came from the biogenic credits and the methane emissions were avoided by diverting food waste from landfills. The impact of avoided methane emissions is dramatic, as this gas traps heat more than 20 times as efficiently as \( \text{CO}_2 \);\(^{31}\) these avoided emissions are credited as negative \( \text{CO}_2\)-eq emissions in accordance with previous work.\(^{2,26}\) Biogenic credits for the VFA upgrading pathways were between 69 and 73 g
CO₂-eq./MJ which were very similar to the combustion emissions during vehicle or jet fuel used for each product (70–75 g CO₂-eq./MJ), offsetting these emissions. These emissions are accordingly omitted from Figure 7, unlike those of the petrofuels.

We explored the key drivers of GHG emissions for each scenario and found that carbon intensities are dramatically affected by assumptions related to food waste management, the counterfactual scenario. Baseline landfill gas (LFG; consists of roughly 50/50 CO₂/CH₄) collection rates were assumed to be 59% (middle bar of each scenario, Figure 7), corresponding to emissions credits between 75 and 134 gCO₂-eq./MJ and final carbon intensities of 22, 22, 28, and 36 gCO₂-eq./MJ for sub-scenarios 3.2, 5.1, 2.Extra, and 1.1, respectively. In this case, carbon intensities of VFA-derived fuels are between 57 and 74% lower than fossil analogs. We also considered a case in which generated methane is captured and flared at an 80% rate (left bar of each scenario, Figure 7), very similar to anaerobic digesters at wastewater treatment facilities but not currently feasible in landfills. Here, the total GHG emissions of the VFA-derived pathways increase to 89, 97, 121, and 156 g CO₂-eq./MJ for sub-scenarios 3.2, 5.1, 2.Extra, and 1.1 respectively because the avoided CH₄ emissions decrease by ~90% in all scenarios. Carbon intensities of VFA-derived fuels under these conditions are higher than those of fossil fuels. If, on the other hand, the LFG collection rate is set to zero (right bar of each scenario, Figure 7), a case when landfill methane emissions are uncontrolled, as is the case with biogas produced by manure lagoons, the total GHG emissions are significantly reduced to −171, −194, −241, and −310 g CO₂-eq./MJ for sub-scenarios 3.2, 5.1, 2.Extra, and 1.1 respectively. The >350% increase in avoided CH₄ emissions in all scenarios drives these charges. The carbon intensities presented herein represent the spread of possibilities for this process and are primarily driven by assumptions regarding landfill gas capture efficacy.

An interesting effect of the credits for avoided emissions from food waste management arising when examining the baseline scenario of 59% LFG capture is that pathways with lower bioblendstock carbon yields achieve larger credits per unit energy. For example, Sub-scenario 1.1 (64.2% C yield) garners a credit of 134 g CO₂-eq./MJ, while Sub-scenario 3.2 (86.8% C yield) garners a credit of only 75 g CO₂-eq./MJ. Figure 7 shows, however, that the biggest positive contributor to total GHG emissions is VFA production, which increases as process carbon yield decreases (Sub-scenario 3.2 < Sub-scenario 5.1 < Sub-scenario 2.Extra < Sub-scenario 1.1), and that this trend more than cancels out the larger avoided emissions credits awarded to scenarios with lower carbon yields. We note that in situ product recovery of VFAs during fermentation can dramatically lower energy requirements for VFA production, further lowering life cycle carbon emissions. An interesting effect of the credits for avoided emissions from food waste management arising when examining the baseline scenario of 59% LFG capture is that pathways with lower bioblendstock carbon yields achieve larger credits per unit energy. For example, Sub-scenario 1.1 (64.2% C yield) garners a credit of 134 g CO₂-eq./MJ, while Sub-scenario 3.2 (86.8% C yield) garners a credit of only 75 g CO₂-eq./MJ. Figure 7 shows, however, that the biggest positive contributor to total GHG emissions is VFA production, which increases as process carbon yield decreases (Sub-scenario 3.2 < Sub-scenario 5.1 < Sub-scenario 2.Extra < Sub-scenario 1.1), and that this trend more than cancels out the larger avoided emissions credits awarded to scenarios with lower carbon yields. We note that in situ product recovery of VFAs during fermentation can dramatically lower energy requirements for VFA production, further lowering life cycle carbon emissions. Thus, given baseline LFG capture assumptions, VFA upgrading processes with higher carbon yields also have lower life cycle carbon intensities.

DISCUSSION

Techno-economic and life cycle analysis of the VFA upgrading processes presented herein show that VFA upgrading-derived transportation fuels sourced from food waste have the potential to be economically profitable and proffer lower carbon intensity than equivalent petrofuels, given the current state of incomplete landfill methane off-gas capture. Figure S8 shows that the profitability of the various upgrading scenarios also improves as biorefineries are scaled up, with a minimum VFA purchase price increasing by $0.17-$0.20/kg as scale increases from 26.6 to 200 tons VFA/day. Figure S9 shows that VFA production drives GHG emissions of VFA-derived fuels and that natural gas heating required for the extraction and distillation of VFAs from fermentation broth is the major driver of VFA production GHG emissions. Other separation technologies, such as membrane-based processes, offer the potential to reduce energy demand, lowering greenhouse gas emissions of the entire upgrading process.

This work proffers a high-throughput screening strategy that enables the determination of the relative merits of diverse bioblendstock upgrading schemes which have promise to satisfy societal needs currently fulfilled by fossil resources. We have applied this approach to upgrading of wet waste-derived volatile fatty acids to liquid transportation fuels through the development of the VFA Upgrading to Liquid Transportation Fuels Refinery Estimation (VULTURE). The model validation results presented in this work show that the VULTURE’s combination of simple approximations of catalytic and separations unit operation efficiencies and fuel blending predict the performance of rigorously modeled process units and experimentally measured fuel properties with a high degree of accuracy, enabling the identification of a handful of scenarios with high carbon yields from hundreds of possible options. Techno-economic and life cycle analyses show that these processes are economically feasible and have life cycle carbon intensities less than half that of conventional petrofuels, assuming...
conventional landfill gas capture efficacy. Refinement and expansion of this technique to simultaneously analyze hundreds of operational choices encompassing all stages of biomass upgrading, from the comparison of various feedstocks and processing methods to end uses, for applications in crucial areas such as fuels and materials can inform the development of optimized upgrading processes for heterogeneous renewable feedstocks to high-value products.

Limitations of the study

The approach developed in this work, a systematic, high-throughput screening strategy for biomass upgrading configurations and end uses, serves as a useful tool to discern optimal upgrading strategies for heterogeneous streams, but alterations must be implemented in order to extend it to many non-VFA inputs. Two crucial aspects of VFA feedstocks make the strategy particularly applicable: (i) the molecular content of VFA influent streams is precisely defined and (ii) reaction products from each unit operation can be predicted with high precision. Many biomass streams do not meet these two criteria. For example, the molecular content of oils produced by catalytic fast pyrolysis is not entirely characterized \(^{12,13}\) and the number of possible reactions in upgrading of syngas \(^{45,46}\) or methanol \(^{14,47}\) over zeolites is too high to enumerate. A lumping approach such as that utilized by Pecha et al. for catalytic fast pyrolysis \(^{13}\) or in the petrochemical industry \(^{49}\) can be applied to allow for high-throughput analysis of upgrading in such complex systems. Important objective functions other than product bio-carbon content, such as economic metrics or carbon intensity, can also be incorporated using simple metrics from these fields. In the case of this study, the similar prices and carbon intensities of all petrofuels being replaced caused economic viability and carbon intensity to scale with overall process carbon yield, but this will not be the case for systems in which prices and carbon intensities of potential products are not similar.

Comparison of measured fuel properties with those predicted by VULTURE (vide supra) shows that, although most fuel properties are successfully modeled by VULTURE, further improvements to the models used in this work can be made. The fuel property prediction in VULTURE most in need of improvement is boiling behavior, as the T90 values in Figure 4A were significantly underpredicted by the model and the boiling point curves for gasoline and jet fuel in Figures S3A and S3B did not conform to drop-in compliant boiling point curve ranges. Comprehensive addressing of this issue would involve simulating the entire boiling point curve of a mixture using a method such as that utilized by Heyne and colleagues \(^{19,49}\) and, for gasoline and jet fuel, setting multiple boiling point criteria (e.g., initial boiling point, T10, T30, T50, T70, T90, and final boiling point) \(^{50}\) according to fuel operability standards. More rigorous models for other important fuel properties, such as the octane number relationship for alkanes developed by Ghosh et al. \(^{51}\) or the freezing point blending models presented by Coutinho et al. \(^{52}\) or Boehm et al. \(^{53}\) could be employed in VULTURE as well, but the accuracy of these property predictions shown in Figure 5 shows that incorporating these more rigorous methods is not crucial.

The scope of process non-idealities, unit operations, and product applications considered could also be broadened to expand the utility of VULTURE. Detailed process simulations (vide supra) revealed that light ketone losses to the post-ketonization aqueous phase resulted in appreciable overall yield decreases (up to 16.4%, Figures S and S5). This phenomenon could be captured by VULTURE through the development of correlations for ketone partitioning into water based on the carbon chain length and incorporation of these correlations into the program. Additionally, a distillation of the aqueous phase could be added to the process in order to recover and upgrade light ketones, increasing carbon yield at the cost of requiring more energy input. Expansion of the upgrading processes and product end users considered by VULTURE could also broaden the scope and applicability of the high-throughput analysis utilized in this work. Of particular interest are upgrading processes to form sustainable aviation fuel, as demand for aviation fuel is expected to increase throughout this century while the electrification of ground transportation will decrease demand for gasoline and diesel. \(^{54,55}\) Catalytic condensation/dehydrogenation and hydrodeoxygenation of short-chain (C\(_3\)-C\(_7\)) ketones derived from VFA ketonization has been shown to create a mixture of branched and cyclic alkanes with favorable jet fuel properties. \(^{2,56}\) Incorporation of options such as this into VULTURE would enable targeting of more specific objective functions such as the maximization of aviation fuel production. The n-alkanes produced in this work can also be isomerized using readily available technology; incorporation of hydroisomerization into VULTURE would also broaden the applicability of this approach for SAF by allowing for the production of alkane mixtures with lower boiling points than neat n-alkanes. The scope of considered applications could also be readily expanded to other important fuel and non-fuel applications, such as the production of marine fuel \(^{57}\) or alkene monomers suitable for polymer production, which can be formed from acid-catalyzed alcohol dehydration. \(^{58-61}\)
STAR METHODS
Detailed methods are provided in the online version of this paper and include the following:

- KEY RESOURCES TABLE
- RESOURCE AVAILABILITY
  - Lead contact
  - Materials availability
  - Data and code availability
- METHOD DETAILS
  - Contents of synthesized fuel mixtures
  - Fuel property predictions and application specification limits
  - Slaughterhouse waste anaerobic digestion
  - Fuel property measurements
  - Process simulation and techno-economic analysis
  - Life cycle analysis

SUPPLEMENTAL INFORMATION
Supplemental information can be found online at https://doi.org/10.1016/j.isci.2022.105384.

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AUTHOR CONTRIBUTIONS
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DECLARATION OF INTERESTS
DRV is Chief Technology Officer and EDC is an employee of Alder Fuels, LLC.

INCLUSION AND DIVERSITY
We support inclusive, diverse, and equitable conduct of research.

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STAR METHODS

KEY RESOURCES TABLE

| REAGENT or RESOURCE | SOURCE | IDENTIFIER |
|---------------------|--------|------------|
| Deposited data      |        |            |
| GitHub repository with VULTURE code and component fuel property data (https://github.com/jacob-h-miller/VULTURE) | This paper | https://doi.org/10.5281/zenodo.7143486 |
| Software and algorithms |    |            |
| MATLAB R2019b        | The Mathworks, Inc. | https://www.mathworks.com/products/matlab.html |
| Aspen Plus           | Aspen Technologies, Inc. | https://www.aspentech.com/en |
| Argonne GREET Model  | Argonne National Laboratory | https://greet.es.anl.gov/ |
| Other               |        |            |
| CAHN TG-131 Thermogravimetric Analyzer | CAHN | N/A |
| Agilent 7890A Gas Chromatograph | Agilent Technologies, Inc. | https://www.agilent.com/en/product/gas-chromatography/gc-systems |
| VUV Analytics VGA 101 | VUV Analytical | https://vuvanalytics.com/vga-101-detector/ |

RESOURCE AVAILABILITY

Lead contact
Further information and requests for resources and reagents should be directed to and will be fulfilled by the lead contact, Jacob Miller (jacob.miller@nrel.gov).

Materials availability
This study did not generate new unique reagents.

Data and code availability
- Compound-specific fuel property data have been deposited on our GitHub repository (https://github.com/jacob-h-miller/VULTURE) and are publicly available as of the date of publication. DOIs are listed in the key resources table.
- All original code has been deposited on our GitHub repository (https://github.com/jacob-h-miller/VULTURE) and is publicly available as of the date of publication. DOIs are listed in the key resources table.
- Any additional information required to reanalyze the data reported in this paper is available from the lead contact upon request.

METHOD DETAILS

Contents of synthesized fuel mixtures
We physically mixed and tested fuel properties of five fuel mixtures (two gasoline samples, “Gasoline 1” and “Gasoline 2”; one jet sample, “Jet”; and two diesel samples “Diesel 1” and “Diesel 2”) generated by VULTURE to evaluate the robustness of the fuel property predictions used herein. Gasoline 1 comes from Sub-scenario 1.1, Gasoline 2 comes from Sub-scenario 5.1, Jet comes from Sub-scenario 3.2, Diesel 1 comes from Sub-scenario 5.1, and Diesel 2 comes from Sub-scenario 2.Extra (Figure 3, Table S3). Content of each mixture is specified by an optimum sub-scenario shown in Figure 3 excluding Diesel 2, which is the hydrocarbon diesel fuel predicted by VULTURE to have the highest bio-content of all evaluated fuels (61 wt %, Sub-scenario 2.Extra, Table S3) and was included to probe the validity of VULTURE’s alkane diesel fuel property predictions. Precise compositions of each mixture are listed in Table S4. Substantial efforts were made to acquire the exact molecules dictated by VULTURE, but lack of availability of some alcohols at significant volumes caused us to make isomer substitutions in some cases (see Table S4).
Fuel property predictions and application specification limits

A summary of all equations used to predict fuel mixture properties are listed in Table S1. Boiling points, melting points, and water solubilities of individual alcohols and alkanes were determined from values predicted in the US Environmental Protection Agency’s EPISuite.\(^6\) Raoult’s Law for ideal mixtures was used to predict boiling points (Table S1). Vapor pressures of all fuel components used in these calculations come from the NIST Webbook,\(^6\) the NIST-TRC Web Thermo Tables,\(^6\) or the Springer Materials database.\(^6\) Flash points of bio-derived alkanes were taken from listed values from CAMEO Chemicals,\(^6\) while flash points of bio-derived alcohols were calculated according to the correlation published by Prugh:\(^6\)

\[
T_{\text{flash}} = \frac{T_{\text{boil}}}{1.3611 - 0.0697 \ln(X_{\text{St}})} \quad \text{(Equation 4)}
\]

\[
X_{\text{St}} = \frac{83.8}{4n_C + 4n_S + n_H - 2n_O - n_X + 0.84} \quad \text{(Equation 5)}
\]

In the Prugh equation, \(T_{\text{flash}}\) and \(T_{\text{boil}}\) are in Kelvin and \(n_C, n_S, n_H, n_O,\) and \(n_X\) are the number of carbon, sulfur, hydrogen, oxygen, and halogen atoms in the compound’s molecular formula. Energy density (lower heating value, LHV, in MJ/kg) is calculated from higher heating value (HHV, in MJ/kg) according to ASTM D240:\(^6\)

\[
\text{LHV} = \text{HHV} - (0.2122 \times 100 \times w_C) \quad \text{(Equation 6)}
\]

LHVs were calculated using ASTM D240 and correlations developed for higher heating values.\(^7\)\(^-\)\(^12\) Higher heating values (HHV, in MJ/kg) were calculated as averages of correlations developed by Lloyd and Davenport,\(^7\) Dulong, and Boie:\(^1\)\(^2\)\(^-\)\(^3\)

\[
\text{HHV}_{\text{LloydDavenport}} = 100 \times (0.3578w_C + 1.1357w_H + 0.059w_N + 0.1119w_S - 0.0845w_O) \quad \text{(Equation 7)}
\]

\[
\text{HHV}_{\text{Dulong}} = 100 \times (0.336w_C + 1.418w_H + 0.094w_P - 0.145w_O) \quad \text{(Equation 8)}
\]

\[
\text{HHV}_{\text{Boie}} = 100 \times (0.3515w_C + 1.1617w_H + 0.06276w_N + 0.1046w_P - 0.1109w_O) \quad \text{(Equation 9)}
\]

In these equations, \(w_C, w_H, w_N, w_S, w_P,\) and \(w_O\) are weight fractions of carbon, hydrogen, nitrogen, sulfur, phosphorous, and oxygen in each compound. Viscosities of upgraded bioblendstock molecules were determined at 25°C (used for gasoline) from the EPA’s TEST software,\(^7\) while viscosities at ~40°C (diesel) were taken from the NIST-TRC Web Thermo Tables.\(^6\) Cetane and research octane numbers of all components were obtained from the University of Massachusetts at Lowell Energy and Combustion Research Laboratory Combustion Database.\(^7\)

Flash points of mixtures containing only hydrocarbons were calculated using the blending index-dependent formula of Wickey and Chittenden\(^7\) (Table S1). Blending indices of individual components \((B_i)\) are dependent on flash points of these components in units of absolute temperature \((T_{FP,i})\):

\[
B_i = 10^{-6.1188 + 2418 \frac{T_{FP,i}}{T_{FP,i} + 463}} \quad \text{(Equation 10)}
\]

Flash points of mixtures containing oxygenates or oxygenates and blends of hydrocarbons were calculated using the similar correlation introduced by Torabian and Sobati (Table S1), where blending indices of individual components are also dependent on flash points:\(^7\)

\[
B_i = T_{FP,i}^{-0.0246} \quad \text{(Equation 11)}
\]

Energy density, melting point, and water solubility of mixtures were calculated as mass-weighted averages of individual component properties (Table S1). Energy released during combustion depends only on the strength of bonds in a molecule, which does not change with mixing, so mass-weighted averaging is suitable for mixture behavior. Hwang et al.\(^7\) found that mixture freezing points are difficult to capture in
models, but that mass-weighted averaging is usually accurate or overestimates melting temperatures; since overestimation of melting points makes predictions of fuel applicability overly conservative, we use this method. Similarly, modeling water solubility using mass-weighted averaging assumes no favorable interactions between water-insoluble fuel molecules that would further decrease water solubility. This method also yields overly conservative fuel applicability limits and is thus also useful. Cetane and octane numbers of mixtures were calculated as mole fraction weighted averages of individual component properties, as has been demonstrated previously. Finally, mixture viscosities were calculated using the Grunberg-Nissan equation (Table S1).

Table 1 lists fuel properties of clay-treated diesel, Jet A, and RBOB gasoline. Property limits for all fuel types (Table 1) are derived from appropriate specifications. We note that specifications are not established for water solubility of jet fuel and flash point, viscosity, melting point, and water solubility of gasoline.

Slaughterhouse waste anaerobic digestion
VFA production in batch mode was performed in 150 mL anaerobic gastight vials at an initial wet waste solids loading of 5% (w/v) and inoculated with fresh activated sludge at 10% total volume. Cultivations were performed at 35°C in a rotary shake incubator with agitation set at 250 rpm, and methanogenesis was inhibited by a single addition of iodoform (Sigma Aldrich, St. Louis, MO, USA) at a concentration of 48 mg/L. Slaughterhouse wastes (JBS Foods, Greeley, CO, USA) were grinded, prepared at different ratios, and inoculated with either acidogenesis or methanogenesis sludge from the two-stage anaerobic digestion system located at the Metro Water Recovery (Denver, CO, USA).

Samples were taken regularly, solids were separated through centrifugation, and supernatant was filtered through a 0.20 μm membrane filter and stored at –20°C until analysis. Concentrations of VFAs were determined by High-Performance Liquid Chromatography (Agilent Technologies, Santa Clara, CA, USA) using a Diode Array Detector (Agilent Technologies). Lactic, formic, acetic, propionic, and butyric acid quantifications were performed using an HPX-87H resin-based column (Bio-Rad, Hercules, CA, USA). Separation was performed with 0.01N H2SO4 at a flow 0.5 mL min⁻¹ using a two-step temperature ramp of 30°C and 55°C at 0 and 19.1 min, respectively. Pentanoic, hexanoic, heptanoic, octanoic, nonanoic, and decanoic acid quantifications were performed using an C18(2) column (Luna, Phenomenex, Torrance, CA, USA). Separation was performed at 60°C at a flow of 0.8 mL min⁻¹ using a gradient with 20 mM H3PO4 and acetonitrile as follows: 80:20 (0, 2 min), 70:30 (5 min), 40:60 (5.01, 15 min), 80:20 (16, 20 min).

Fuel property measurements
Distillation curves of blendstocks and blended fuels were simulated using thermogravimetric analysis (TGA). TGA was utilized for simulated distillation rather than gas chromatography as many fuel components in this work are oxygenates and would not be accurately estimated using standard ASTM methods based on hydrocarbon fuels. Analyses were performed using a CAHN TG-131 TGA set to ramp from ambient temperature (~22°C) to 550°C at a constant rate of 50°C/min in a nitrogen atmosphere at flow rate of 60 sccm. Distillation accuracy was established using a hydrocarbon standard designed for verifying ASTM D86 distillation values (Accustandard ASTM-P-127-01).

Flash point, density, heating value, melting point, and viscosity measurements followed ASTM International methods and are listed here: flash point (ASTM D6450-16a(21); density (D4052-18a); heating value (D240-19); melting point (D5972-16); viscosity at 25 and 40°C (performed by Southwest Research Laboratory, ASTM D445-21e1); viscosity at –40°C (ASTM D7042-21). Water solubility was approximated using a similar procedure to that previously published. Each blendstock was added to DI water at a volumetric ratio of 1:5 and blended with a vortex mixer. The solution was allowed to separate for 24 h at ambient temperature (~22°C). The water layer was then removed and analyzed by gas chromatography with vacuum UV spectroscopy for quantitation of solubilized organics. Analysis was conducted with an Agilent 7890A GC coupled with a VUV Analytical VGA 101 detector. A volume of 0.1 μL was injected into a split/splitless inlet set to 250°C and a split ratio of 1:20. Compounds were separated using an Rxi-1 MS column (polydimethylsiloxane, Restek) of dimensions 30 m x 0.25 mm x 0.25 μm with a helium carrier gas at a flow rate of 1.0 mL/min. The GC oven temperature was held at 35°C for 10 min, then ramped to 200°C at 7°C/min. The VUV transfer line and flow cell were held at
250°C. A gravimetrically prepared standard of 2-propanol in water was used to establish the alcohol response factor of the VUV detector as well as precision and linearity of the GC-VUV analysis.

Indicated cetane numbers were measured with NREL’s Advanced Fuel Ignition Delay Analyzer (AFIDA) instrument using ASTM D8183-18. Research octane numbers of small-volume fuel samples were determined using a recently developed methodology with the same device, where RON can be quantified to a SE of 1.3 and r² of 0.94 with as little as 40mL of sample.

Process simulation and techno-economic analysis
Techno-economic models of selected VFA upgrading sub-scenarios were developed to quantify economic potential. These models utilized mass and energy balances from a thermodynamically-rigorous process model of VFA upgrading and separation (Aspen Plus v10) to perform a discounted cash flow rate of return (DCFROR) analysis. Each model considered a feedstock of mixed VFAs which undergo a series of catalytic upgrading and separation steps to yield a variety of bioblendstocks. Mixed VFAs are assumed to be sourced from the anaerobic digestion of food waste; however, due to the number of different VFA production and separation schemes which might be utilized to produce the mixed VFA feedstock, many of which are at a low technology readiness level relative to the upgrading technologies, the decision was made to exclude VFA production and separation from the scope of the TEA. Accordingly, we solve for a maximum VFA purchase price which would achieve a 10% internal rate of return for the process, signifying economic viability. Fuel products are sold at values equivalent to the 7-year average market values. and biofuel policy incentives such as RIN credits are not considered. Facility scale is set at 26.6 tons of VFAs per day, determined by assuming VFAs are generated from food waste (limited by regional availability at 250 wet tons/day) at a VFA yield of 0.45 kg/kg food waste. By framing the assessment in this way, a benchmark for targeting VFA production costs in the context of fuel production is established. Maximum VFA purchase price is also reported for a variety of production scales to make these results applicable to alternative VFA sources (Figure S8).

The upgrading strategies vary by case and are shown in Figures 2, S1, and S10. In brief, the mixed VFAs undergo a ketonization reaction to increase the average chain length of the fuel precursors. VFAs can be sent directly to ketonization or separated by distillation into light and heavy cuts; regardless, the first upgrading step for all VFAs is ketonization. Following ketonization, CO₂ is flashed off at sufficiently cold temperatures to recover the majority of any volatile ketones present and water is decanted from the organic phase. Recovered ketones can then be upgraded by hydrogenation to alcohols or alkanes depending on the method specified by VULTURE. Details of conditions for each processing step are below. Mass and energy balances from each process model are used to inform the capital and operating expenditures for building and operating the described VFA upgrading facility.

The techno-economic analysis (TEA) utilizes process models developed in Aspen Plus in tandem with a discounted cash flow rate of return (DCFROR) analysis to quantify the economic viability of the process. Since the front-end VFA production is not included, a maximum VFA purchase price is determined such that the net present value of the biorefinery is zero for an internal rate of return (IRR) of 10%. Direct and indirect cost factors are applied as is consistent with prior works. The biorefinery is assumed to be financed at 40% equity and have a plant life of 30 years; additional financial parameters relevant for the DCFROR are provided in Table S7. Details for each unit operation of the process model draw on prior works and will be described briefly here, with key parameters supplied in Table S6. A breakdown of capital expenditures for each case is provided in Table S8.

VFA production
VFA production is not explicitly included in the TEA model. However, high-level assumptions are made in order to model the processes at a scale consistent with producing the VFAs from food waste at a rate of 250 wet tons of food waste per day. These assumptions are consistent with prior analyses and result in a VFA feed rate of 26.6 tons per day.

Ketonization
VFAs are heated to a temperature of 365°C through two heat exchangers utilizing reactor effluent heat in addition to a hot oil system. In the ketonization reactor, binary reactions of all VFA components present occur. The yields of each ketone produced from the given VFA profile are predicted according to the
methodology outlined in Note S1. The TEA model groups ketones of the same carbon length into one component rather than modeling isomers, as is consistent with prior work. No formation of side products is considered. The reactor effluent is cooled and CO₂ produced in ketonization is flashed off. Volatile ketones are recovered by cooling the vapor stream using chilled brine, and the resulting liquid is decanted to remove the aqueous phase. Some shorter-chain ketones are lost with the aqueous phase; the remainder then proceed to the next upgrading step, which varies by scenario and may consist of hydrogenation to alcohols or hydrodeoxygenation (HDO) to alkanes.

**Hydrogenation to alcohols**

Hydrogenation to alcohols uses less severe conditions than HDO to hydrogenate the ketone group without completely removing it. Ketones are first subjected to an additional drying step using a molecular sieve before being heated and fed to the reactor along with the required H₂. The effluent of the reactor is cooled and flashed to separate unreacted hydrogen which is recycled back to the reactor. A purge stream is also taken from the recycle stream to prevent buildup of other light components such as CO₂. The liquid stream from the flash consists of finished alcohols which can may be used as a direct bioblendstocks (Sub-scenarios 3.2, 1.1, 2. Extra) or further separated to light and heavy alcohols (scenario 5.1).

Assumptions regarding the hydrogenation reactor are largely based on patent literature but are also consistent with comparable published data. One assumption that should be specifically noted is that the TEA model assumes 100% conversion of ketones to alcohols in a single pass. If this is not achieved, unreacted ketones would likely have to be separated from the mixture of alcohols prior to fuel blending, which could not be achieved by simple distillation. In this case, a more complex separations scheme would be required, adding significant cost to the process. While 100% conversion is not unreasonable (with 93% conversion and 86% selectivity demonstrated in patent literature), it is important to note this assumption.

**Hydrodeoxygenation**

Ketones can alternatively undergo a more severe catalytic upgrading step to yield alkanes which are generally more amenable to blending/replacing hydrocarbon fuels. The process model assumptions regarding HDO are consistent with prior work.

**Utilities and storage**

Utility requirements for the process, including grid electricity, cooling water, steam, hot oil, and storage are accounted for the model. Steam and hot oil requirements for the process are met by with natural gas, with process off-gases also utilized. Off-site wastewater treatment costs are calculated on a chemical oxygen demand (COD) basis using a $/kg COD cost factor from literature.

**Life cycle analysis**

The Greenhouse gases, Regulated Emissions, and Energy use in Technologies (GREET) model, used to compute process carbon intensities, is a publicly-available model developed with the support of the U.S. Department of Energy that is regularly used to evaluate the life cycle energy and environmental impacts of fuels and chemicals. The functional unit for this study is one megajoule (MJ) of fuel output and GHG results are presented in terms of grams of CO₂-equivalent per MJ of biofuel produced (g CO₂-eq./MJ). Emissions of carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O) are included in the scope with global warming potential calculated on a basis of the IPCC Fifth Assessment Report values for the 100-year time horizon, 1, 30, and 265 g CO₂-eq./g, respectively. Figure S11 describes all the steps of the system boundary of the biofuel production pathways considered here and the comparison with their conventional petroleum-derived products. We included the impacts from each step of the biofuel supply chain starting from feedstock transportation and distribution, VFA conversion and upgrading in the bio-refinery, fuel transportation and distribution, and finally fuel combustion during vehicle use.

Degradation of food waste in the landfill and subsequent production of carbon dioxide and methane are estimated using GREET which is consistent with the methodology presented at the US EPA’s WARM model. U.S. average landfill capping, gas collection, and flaring is also assumed for calculating the emissions from business-as-usual landfill gas management. We assumed that the landfill gas (LFG) collection rate is about 59% in our base case, and that the landfill gas is 50%/50% mixture (V/V) CH₄ and CO₂.
We leveraged the material and energy input presented in Huq et al. for VFA production, while the material and energy inputs for upgrading of VFA to hydrocarbons were developed based on the Aspen Plus simulation results (vide supra). Details on the material and energy inputs for the upgrading processes are presented in Tables S9–S11. We used the U.S. average electricity generation mix and assumed the natural gas used is produced in the U.S. Tables S10 and S11 summarize some of the assumptions used for feedstock transportation and fuel transportation and distribution available in the GREET model. We assumed that the feedstock logistics used for VFA upgrading are the same as yellow grease and used the same procedure as Ou et al.

Figure S9 shows the GHG emissions breakdown of VFA production from food waste and upgrading. VFA production includes emissions from transportation of feedstock, fermentation, and separation processes. Residual solids (precipitating carbonates and biosolids) were the two main byproducts from fermentation. The solid waste streams contain 11% (carbonates) and 46% (biosolids) of waste-derived carbon and were considered landfilled. We assumed that the solid waste has similar carbon stability to standard anaerobic digestate. Therefore, 20% of carbon in the solid wastes was assumed sequestered, while for the biosolid, a small amount of CH₄ (0.05 g CH₄/kg C) is emitted during landfilling of the solid waste. No CH₄ emissions were considered for the carbonates as we assume that carbonates are stable once landfilled. These emission values were very small as the amount of residual solids was inconsequential.