# A SYSTEMS LEVEL ANALYSIS OF ETHANOL UPGRADING TO MIDDLE DISTILLATES

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## ARTICLE

### A SYSTEMS LEVEL ANALYSIS OF ETHANOL UPGRADING STRATEGIES TO MIDDLE DISTILLATES

Juan-Manuel Restrepo-Flórez[a], Joonjae Ryu[b], Dustin Witkowski[a], David Rothamer[a], and Christos T. Maravelias[c,d]

We systematically study the upgrading of ethanol toward middle distillates with desired properties. To survey the large design space, we introduce a novel superstructure-based optimization framework integrating process design and fuel formulation. We show that biorefineries that produce middle distillates by upgrading lignocellulosic ethanol can have an energy return on investment (EROI) greater than 1. Additionally, we show that technological improvements can lead to significant increases in EROI. Furthermore, trade-offs between fuel properties and biorefinery profitability are established, showing how process economics are strongly influenced by fuel properties. In the case of diesel, the feasibility of producing high cetane number biofuels is demonstrated, coupled with a discussion of the technological requirements and costs to produce these superior fuels. It is also shown that the minimum fuel selling price (MFSP) can be reduced by increasing the biorefinery complexity. Finally, we discuss the possibility of satisfying current and projected middle distillates demand in the U.S. using biofuels produced by ethanol upgrading, and we estimate the potential $CO_2$ mitigation of these technologies.

### Broader context

Ethanol has been established as the major biofuel, with a production capacity in the U.S. of ~1.1 million barrels per day. However, ethanol cannot be blended with middle distillates which, coupled with current projections on declining gasoline demand, has prompted research on ethanol upgrading to components or blends with properties similar to those of middle distillates. Ethanol upgrading to middle distillates is important because the sectors where middle distillates are consumed (aviation and freight) are hard to electrify. Currently, there exist many chemistries and catalysts for the transformation of ethanol into a broad palette of components. However, designing ethanol upgrading strategies toward middle distillates remains challenging because of the large design space and the need to simultaneously consider process economics and product properties. Some open questions include: (1) the energy requirements of the upgrading process; (2) the interactions among fuel properties, processes, and profitability; (3) the effect of process complexity on profitability; and (4) the impact on the fuel supply and $CO_2$ mitigation. Accordingly, we herein propose a systems-level framework to address these questions.

## INTRODUCTION

Currently, U.S. consumption of liquid transportation fuels is approximately 13 million barrels per day[1], accounting for nearly 28% of the national greenhouse gas emissions[2]. Most of this demand is satisfied by fossil fuels. In this context, the large-scale deployment of biofuels has the potential to mitigate the negative impacts of fossil fuel consumption[4]. This approach is especially important in the case of middle distillates, which are primarily consumed in aviation, hauling, and maritime transport. These sectors have been identified as difficult-to-decarbonize, mainly because their electrification is challenging and will likely remain so in the upcoming decades[5,6].

Furthermore, the current fuel consumption forecasts project a significant middle distillates demand increase in the next 30 years[4]. A promising platform, directly addressing these challenges relies on the upgrading of ethanol[7–10]. This platform has three major advantages. First, it can use available infrastructure for ethanol manufacturing to produce 1.1 million barrels per day in the U.S[11]. Which is important, considering that the domestic ethanol demand is already satisfied[12] and it is expected to decrease, leading to a surplus of ethanol in the market[9,13]. Second, the ethanol upgrading enables the production of fuels in the whole distillation spectrum, including middle distillates. Third, ethanol upgrading strategies can exploit developments in ethanol chemistry to produce better fuels with tailored properties[7,8,10].

Despite the benefits above, finding optimal ethanol upgrading strategies is challenging because there is a large set of alternatives whose systematic evaluation is non-trivial. For example, there are more than twenty chemistries that can be used to upgrade ethanol. These chemistries can be employed in multiple serial and parallel arrangements, and each chemistry can be realized using several

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catalysts[7,14]. Additionally, it is necessary to simultaneously consider fuel properties. Consequently, researchers have mainly relied on their independent understanding of chemistry, fuel properties, and process synthesis to design and analyse new upgrading strategies[14–17]. This ad hoc approach has left two fundamental questions unaddressed regarding the production of middle distillates from ethanol: is there a net energy gain in the production of these biofuels (i.e., EROI>1)? and will green-house gas emissions be reduced by producing these fuels? Furthermore, since the relation between fuel properties and economics is unclear, the cost of tailoring fuel properties is not well understood.

To address the critical questions above, we propose a systems-level framework that enables the simultaneous assessment of all alternative strategies while considering their capital and operating costs, as well as the properties of the fuels produced. While work towards the formulation of such a framework for ethanol upgrading is limited[18], recent research in biorefinery synthesis has resulted in methods and information that can be readily used[19,20,29–33,21–28]. In particular, we highlight works in superstructure-based process synthesis[19–22,24], enabling the simultaneous analysis of multiple alternatives, and those in which fuels properties are considered explicitly[18,27–31,34].

In this work, we systematically study the upgrading of ethanol toward middle distillates (jet fuel and diesel). Our work sheds light into four fundamental issues not comprehensively addressed in the available literature, including the work of Restrepo-Flórez and Maravelias[18]: (1) the energy requirements of ethanol upgrading biorefineries, (2) the relation among fuel properties, composition, and profitability, (3) the role of biorefinery complexity, and (4) the extent to which the designed biofuels can satisfy forecasted fuel demands and mitigate $CO_2$ emissions. These questions are addressed systematically considering a representative state-of-the-art design space including 22 chemistries and 113 catalysts. To perform this analysis, we rely on a new superstructure-based optimization framework, which allows estimating the capital and operating costs of potential biorefineries while ensuring that the produced fuels display desired properties. In contrast with the work of Restrepo-Flórez and Maravelias[18], in which a reduced designed space was used because extensive simulations were required as an input, in this work we develop a novel framework in which short-cut models are used[35,36]. Therefore, surveying a larger number of alternatives is possible.

# OPTIMIZATION FRAMEWORK

## Problem description

Ethanol upgrading can be described as a sequence of chemical transformations leading to products that satisfy given property specifications. Ethanol is first transformed into a set of chemical species that may undergo further transformations. The products obtained in each transformation can be directed toward other chemistries or the final products. Formally, the problem can be stated as follows:
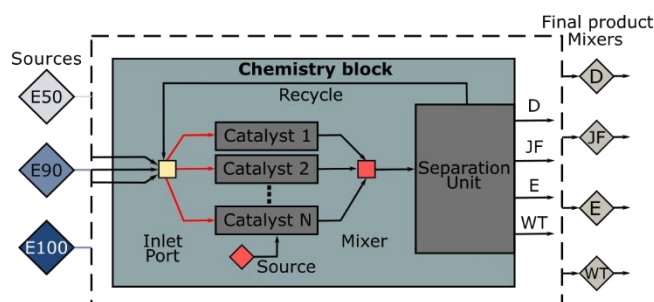
Given:
- A set of chemistries



**Figure 1.** Superstructure architecture. Possible final products include diesel (D), jet fuel (JF), electricity (E), and waste (WT). Ethanol sources: ethanol 50% (mol/mol) (E50); ethanol 89.5% (mol/mol) (E90), and anhydrous ethanol (E100). Red arrows are used to represent the conditioning of streams fed to a catalyst.

- A set of catalysts able to realize each chemistry
- A set of fuel products of interest with specified properties

Find:
- The sequence of chemical transformations
- The catalysts to perform these transformations
- The interconnections between these elements
- The energy consumption associated with the chemistries and catalyst selected

Such that:
- The final products satisfy given property specifications
- An objective function of interest is maximized/minimized

## Superstructure

This problem can be represented using a superstructure, which is a network of all possible process options and the interconnections among them[37–39]. We develop a superstructure architecture containing three major elements (Figure 1): (1) the chemistries used for the transformation of different species, (2) the catalysts that can be used in each of these chemistries, and (3) the separations associated with each chemistry. Catalysts are represented as reactor units, and all catalysts that can realize the same chemistry are grouped into a *chemistry block* (Figure 1). Chemistry blocks can be understood as sections in a facility, with the associated reaction and separation operations. The separations associated with each chemistry block are represented using a unit, which conceptually includes all the operations required to separate the components of interest. Chemistry blocks are interconnected to represent potential upgrading strategies. Through optimization, we find the sequence of chemistry blocks in an upgrading strategy, select the catalyst in each chemistry block, determine the magnitude and composition of connecting stream flows, and estimate the energy consumption in the process. The superstructure architecture is comprehensive in that (1) it allows representing a broad range of design decisions of interest (i.e., catalysts, chemistries, and sequencing of transformations) while considering a large design space; and (2) it contains the typical operations found in a chemical plant (reactions and separations). For a detailed discussion on the superstructure elements see SI-2.
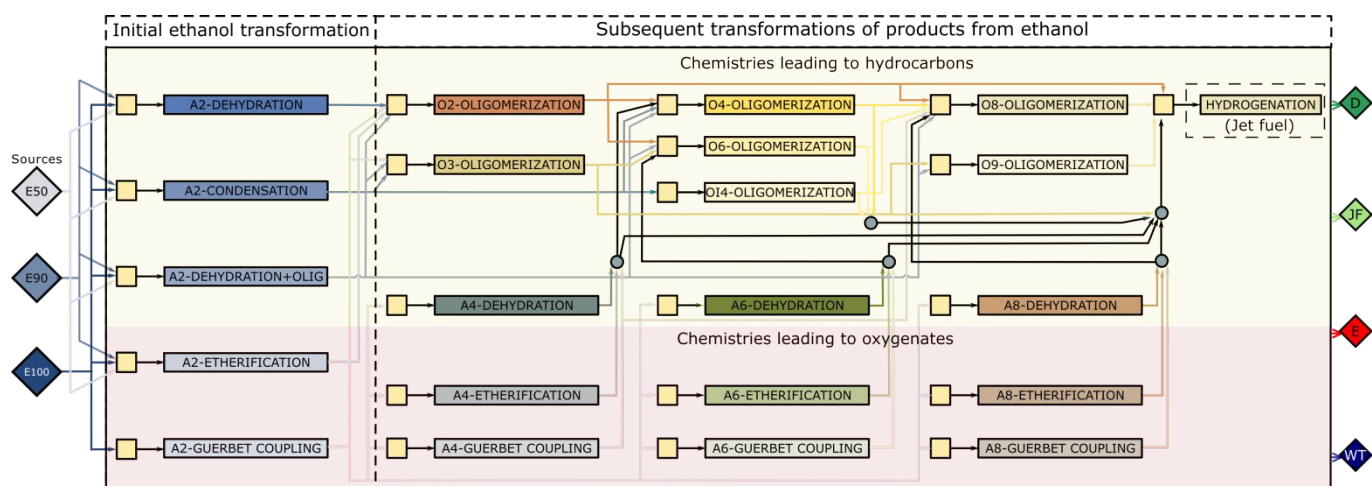
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**Figure 2.** Superstructure containing all chemistry blocks and possible interconnections among them. Sources of ethanol are shown on the left as blue diamonds: 50% (mol/mol) (E50); ethanol 89.5% (mol/mol) (E90), and anhydrous ethanol (E100). Possible products are shown on the right: D: diesel, JF: jet fuel, E: electricity, and WT: waste products. Chemical components are labelled using an alphabetic part to indicate the functional group (A: Alcohols, O: Olefins), and a numeric part for the number of carbons.

## Technology overview

In Figure 2, we present the proposed ethanol upgrading superstructure. Candidate chemistry blocks, sources, and final products are shown along with the potential interconnections among them (See SI-8 for the connectivity matrix). Each chemistry block has the architecture described in Figure 1. Broadly speaking, chemistries associated with direct ethanol conversion can be clustered into two groups depending on products. The first group yields a hydrocarbon product (dehydration, condensation, and simultaneously dehydration and oligomerization); while the second group yields an oxygenated product (Guerbet coupling, and etherification). The products of the first group can be olefins, aromatics, or both; the products of the second group include alcohols and ethers. Products obtained from direct ethanol conversion can be subsequently transformed using other chemistry blocks. For olefins, oligomerization reactions are considered; while for higher alcohols, dehydration to olefins, Guerbet coupling, and etherification are considered. In the case of jet fuel, a hydrogenation chemistry for the transformation of olefins into parafins is included. For each chemistry block, a set of catalysts representative of the state-of-the-art in the literature is selected. These catalysts span a wide range of operating conditions. In total, 112 different catalysts have been included (a brief discussion on the chemistries can be found in SI-1, while details on the operating conditions, catalysts selectivities, and relevant literature are given in SI-5, and SI-6). These chemistries and catalysts result in a diverse palette of chemical species available to tailor the fuel products' properties (See SI-7 for properties of the different components).

## Mathematical model

The problem is formulated as a mixed-integer non-linear programming (MINLP) model (See SI-4 for details). Its simplified mathematical representation is shown in Eq. 1, where the objective is to minimize the fuel selling price. The sales of different fuel products (jet fuel or diesel), and electricity are considered. Costs include capital investment, operating costs corresponding to utilities, catalysts make-up, waste treatment, and feedstocks consumption (See SI-9 for financial parameters).

$$
\min \text{(Minimum Fuel Selling Price)}
$$
$$
s.t. \begin{cases} Process\ model \begin{bmatrix} \text{Mol balances} \\ \text{Utilities calculation} \\ \text{Logical constraints} \\ \text{Capital costs} \end{bmatrix} \\ Fuel\ model \begin{bmatrix} \text{Blending rules} \\ \text{Distillation curve} \\ \text{Composition constraints} \end{bmatrix} \end{cases} \quad (1)
$$

The process model consists of material balances written for superstructure elements, equations to estimate the consumption of utilities, logical constraints based on the superstructure connectivity, and equations to estimate the capital costs of the selected chemistry blocks. The fuel model consists of known and newly developed blending rules establishing a functional relation between the fuel composition and its macroscopic properties, a model for the distillation curve, and a set of constraints on the fuel composition.

An important feature of the model is that it allows estimating the utilities consumed without requiring a detailed flowsheet. To achieve this, the utility demand calculated accounts for (1) the heat to condition the feed to the selected catalysts, (2) the heat consumed

**Table 1**. Fuel property constraints

|  | Type | Jet Fuel | Diesel |
|---|---|---|---|
| CN | Min | - | 40 |
| Density ($\rho$) [kg/m³] | Min | 775 | **820** |
| | Max | 840 | **860** |
| Viscosity ($\nu$) [mm²/s] | Min | - | 1.9 |
| | Max | 8.0 | 4.1 |
| Flash point (FP) [°C] | Min | 38 | 52 |
| Freezing point (FRP) [°C] | Max | -40 | - |
| $T_{JF,5}$ [°C] | Min | 160 | - |
| $T_{JF,10}$ [°C] | Max | 205 | - |
| $T_{JF,100}$ [°C] | Min | 300 | - |
| $T_{D,5}$ [°C] | Min | - | 185 |
| $T_{D,100}$ [°C] | Max | - | 400 |
| Aromatics [%] | Max | 25 | 35 |
| Olefins [%] | Max | 0 | - |
| Oxygenated components [%] | Max | 0 | - |

to maintain isothermal reaction conditions, and (3) the heat duty associated with the required separations. While estimating the first two of these values is simple, the last one is challenging, so we rely on a recently developed targeting approach[35,36] which exploits that the heat duty of a fully thermally-coupled distillation network[40] can be used as a target for distillation.

The fuel model considers density ($\rho$), viscosity ($\nu$), cetane number (CN), flash point (FP), freezing point (FRP), and distillation profile. Additionally, the mass fraction of aromatics, and the content of olefins and oxygenated species in jet fuels are also constrained. (Table 1). Due to the numerical complexity of the models and the lack of adequate surrogates, the cloud point of diesel is not included in the model. However, this property is determined in a post processing using a thermodynamic model (See SI-14)[41]. Linear mixing rules are used to estimate $\rho$, $\nu$, and CN, (i.e., the value of the blend property is calculated as a weighted average of the pure component properties of its constituents). For FP and FRP, we use non-linear blending rules. In the FP case, a new blending rule that is accurate yet computationally tractable is developed (see SI-13). For the freezing point, we implement a recently reported surrogate[42]. The distillation profile is estimated using the true boiling point (TBP) approximation[18,27,43], which relies on the assumption that the components of a blend boil sequentially according to their boiling points. It has been shown that the TBP approximation is effective for the initial screening of fuel blends, even in the presence of oxygenates[27]. Bounds for CN, $\rho$, $\nu$, FP, and FRP are selected based on the American Society for Testing Material (ASTM) standards[44–46] **or, in the case of density for diesel fuel, on the recommendations presented on the World-wide fuel charter[47]**. Bounds for the distillation curve are chosen such that the $T_{f,5}$ and $T_{f,100}$ ($T_{f,x}$: Temperature at which volume fraction *x* of fuel *f* (diesel (*D*) or jet fuel (*JF*)) is evaporated) are similar to fossil fuels, and the ASTM standards are satisfied.

The model is formulated in GAMS and solved using BARON[48] or SCIP[49] solvers. We use computational resources of the High-Performance Computing Center at Princeton University.

## Energy metrics

Here we assess Energy Return on Investment (EROI)[50,51] and Energy Efficiency (EE). The first one is defined as the ratio between the useful energy returned to society over the energy invested (Eq. 2).

The second one is the ratio of the total energy outputs over the total energy inputs (See SI 11 for details). The main difference between these two metrics is that in the *EE* definition the amount of energy originally contained in the feedstock is considered. In both cases, efficiency factors are applied to account for differences in the "quality" between different forms of energy produced or consumed (e.g., heat vs. electricity).

$$EROI = \frac{\sum Energy\ returned\ to\ society}{\sum Energy\ required} \tag{2}$$

$$EE = 100\frac{\sum Energy\ outputs}{\sum Energy\ inputs} \tag{3}$$

## RESULTS AND DISCUSSION

### Energy analysis

In this section, we discuss what is the estimated EROI of middle distillates produced by ethanol upgrading? and how can we improve this value? To answer these questions, we first identify the optimal biorefineries to produce jet fuel and diesel, and then analyse the energy consumption and flows within these systems (Figures 3(a)-(b)). To estimate the energy requirements for ethanol production we rely on literature reports[52]. In all cases, $1 < \mathrm{EROI} < 2$, which suggests that producing middle distillates from lignocellulosic ethanol may lead to a net energy gain. However, the EROIs obtained are significantly lower than those corresponding to typical values for fossil fuels (~20)[50].

In Figure 3, we show the optimal diesel and jet fuel refineries. Including the used chemistry blocks and connectivity among them. In the diesel refinery, ethanol is simultaneously dehydrated and oligomerized producing a blend of aromatics and low molecular weight olefins. These olefins are subsequently oligomerized, increasing their molecular weight, to produce the final fuel blend. The jet biorefinery employs an ethanol Guerbet coupling reaction, followed by alcohol dehydration (butanol and hexanol) and a sequence of olefin oligomerization reactions. A final hydrogenation step transforming the olefins into paraffins is used to ensure that the jet fuel produced is free of olefins. Both in the diesel and the jet fuel biorefineries, two product streams are obtained: a liquid fuel and a stream consisting of by-products. There are two options for the by-product stream: it can be used to produce electricity that is sold to the grid, or it can be used to partially satisfy the biorefinery energy requirements. In the second case a higher EROI is obtained.

It has been suggested that the minimum EROI for a sustainable society is approximately three[51]. Since the current values are below that threshold, innovation in ethanol production and upgrading would be necessary. In Figures 4(a)-(b), we explore the impact that changes in the energy requirements for ethanol production or upgrading would have on the EROI. In ethanol production, these improvements could primarily come from increasing biomass productivity, reducing the environmental footprint of fertilizers, and improving pre-processing technologies (e.g., reducing the energy consumption of biomass pre-processing depots)[52]. For example, it has been estimated that reductions in energy consumption for ethanol production of ~15% can be obtained when biomass yield rises from the current 8.5 Ton/km²-year to 25 Ton/Km²-year[52].

Likewise, reductions in the biomass depot energy consumption could lead to ~10% energy savings[52]. In ethanol upgrading, heat integration and the development of catalysts with high single-pass conversion
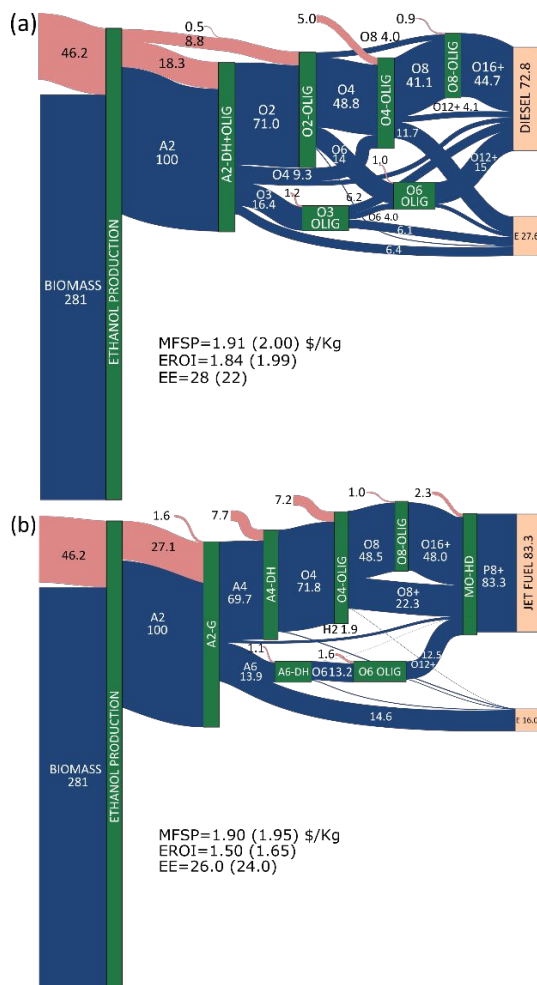


**Figure 3.** Sankey diagrams with the energy flows (MJ) for the optimal biorefineries producing (a) diesel and (b) jet fuel. Pink: primary energy inputs; blue: energy flows within the biorefinery (low heating value). Numbers in parenthesis for MFSP, EROI, and EE correspond to calculations performed assuming that by-products (labelled E) are used to satisfy the biorefinery energy needs. Chemistry blocks (green rectangles) are labelled as follows: alphabetic characters indicate the functional group of the substrate (A: Alcohols, O: Olefins, MO: mixed olefins), and the numerical one is given by its carbon length. The type of chemical transformation is indicated using an abbreviation (DH+OLIG: simultaneous dehydration and oligomerization, DH: dehydration, G: Guerbet coupling, OLIG: oligomerization, HD: Hydrogenation).

could lead to the reduction of the energy demand. Improvements in energy consumption during the upgrading process combined with reductions in the energy demand for ethanol manufacture can lead to an $EROI > 3$. From an economic perspective, the MFSP is strongly influenced by ethanol price, which in turn depends on the feedstock price (e.g., corn, lignocellulosic residues, etc.) and the geographic location of the biorefinery. While these factors are not modelled in detail, we do explore the dependency of the MFSP of the middle

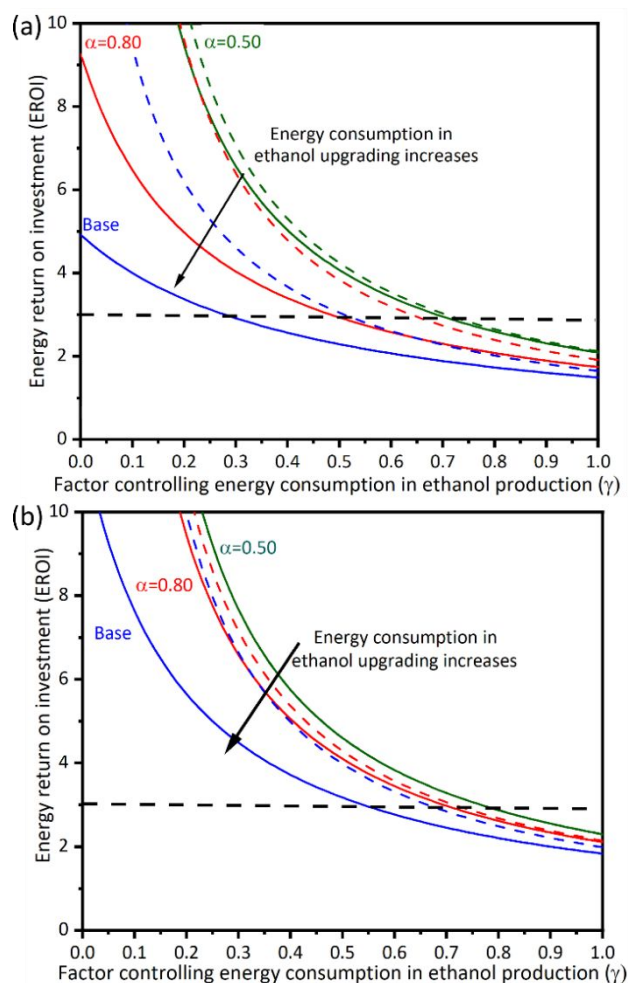distillates produced on the price of the feedstock used for ethanol production (see SI-14).



**Figure 4.** Analysis of the effect of reducing the energy requirements in ethanol production and upgrading on the EROI of biorefineries producing (a) diesel and (b) jet fuel. Continuous lines represent systems where by-products are used to produce electricity that is sold to the grid. Dashed lines represent systems where by-products are used to satisfy the biorefinery energy requirements. Results are shown as a function of two parameters: $\gamma \in (0,1)$, which represents the energy consumed in ethanol manufacture with respect to the reference case (9.58 MJ/l)[52]; and $\alpha \in (0,1)$, which represents the energy consumption in ethanol upgrading with respect to the reference case.

## The role of fuel properties

We seek to understand how different trade-offs impact the design of novel biorefineries and how they can be exploited to improve the biorefinery economics or to produce fuels with better properties.

*Diesel*: First, the effect of relaxing some property constraints on the process economics is studied. We are particularly interested in the impact of $\rho$ and $T_{D,5}$ on the MFSP and the chemistry blocks selected. These variables may significantly impact the economics because a higher yield can be obtained if we relax the constraints on them. Most of the species considered have a lower density than the ASTM
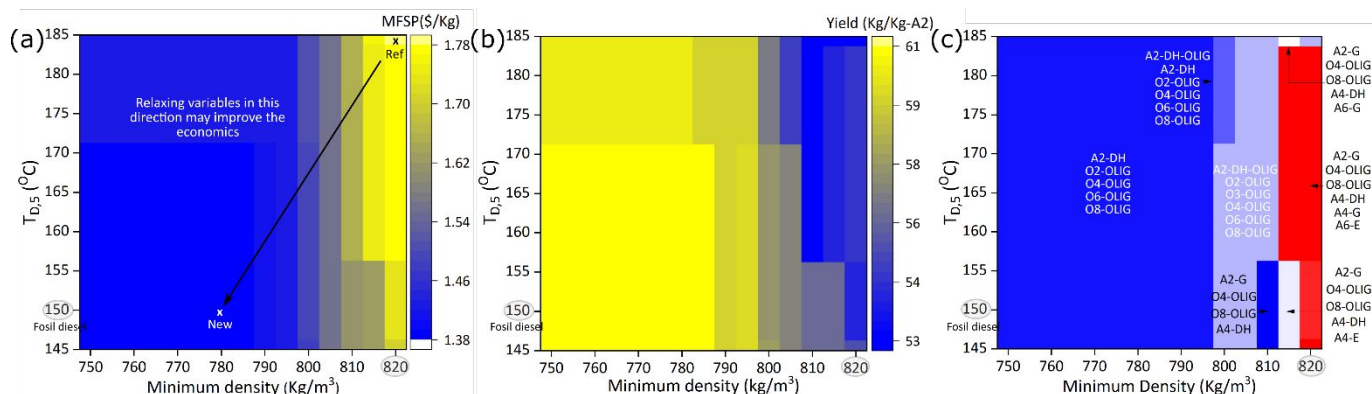
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**Figure 5.** Heat maps showing the effect of relaxing the lower bound on density and the $T_{D,5}$ on (a) MFSP (b) fuel yield and (c) chemistry blocks selected. Chemistry blocks are labelled such that the first character indicates the functional group of the substrate (A: Alcohols, O: Olefins), and the second one its number of carbons. The type of chemical transformation is indicated using an abbreviation (DH: dehydration, G: Guerbet coupling, OLIG: oligomerization, E: etherification).

diesel standard[45] (see SI-7), thus relaxing the constraint on the minimum density broadens the design space. The same effect is expected in the case of $T_{D,5}$, where we have enforced $T_{D,5} \geq 185\ °C$ (Table 1). However, typical diesel may have a $T_{D,5}$ as low as $150\ °C$.

Figure 5 shows the effect of relaxing the lower bound on density and $T_{D,5}$ on the MFSP (Figure 5(a)), the fuel yield (Figure 5(b)), and the selected chemistry blocks (Figure 5(c)). Reducing the lower bound on density from 820 to 780 Kg/m³ reduces the MFSP by ~25%, mainly due to a significant increase in fuel yield (~15%). Likewise, relaxing the constraint on $T_{D,5}$ has a significant, although less pronounced impact. Depending on the fuel properties required, we distinguish seven biorefinery types (Figure 5(c)). In the first three types, which are optimal when the density is below 810 Kg/m³, ethanol is directly transformed into olefins (either ethylene using dehydration, or a blend of aromatics and C2-C4 olefins using simultaneous dehydration and oligomerization), and the molecular weight of these olefins is increased in a sequence of oligomerization reactions. In the other four types, which are optimal when the lower bound on density is higher than 810 Kg/m³, ethanol Guerbet coupling, butanol dehydration, as well as butene and octene oligomerization are employed. They differ by the presence/absence of an etherification or Guerbet coupling reaction for the processing of butanol or hexanol.

We also seek to understand how producing diesel with a higher cetane number would impact the chemistry blocks selected and the economics. Fuels with a high cetane number are more reactive, a feature that may be exploited for thermal management of engine aftertreatment systems enabling reduced $NO_x$ emissions, one of the most pressing challenges associated with the operation of diesel engines[53,54]. Figure 6 shows how diesel blends with superior quality **($CN > 55$)[47] can be produced**. Figure 6(a) shows the MFSP, fuel yield, and chemistry blocks selected, as a function of the minimum cetane number, while Figure 6(b) shows the actual cetane number of the fuels produced and their composition. Two technological platforms appear promising to produce these fuels. If the required cetane number is below 74, a process based on ethanol dehydration and a sequence of oligomerization reactions is required. To reach cetane numbers greater than 74, etherification chemistries are necessary. Accordingly, the mole fraction of ethers increases when $\phi_{D,CN}^{MIN} > 74$ (Figure 6(b)). When $\phi_{D,CN}^{MIN} < 74$, the fuel consists mainly of linear olefins. These results suggest that advances in two areas are critical: (1) the development of olefin oligomerization catalysts leading to the production of linear olefins, which are characterized by a higher cetane number than their branched counterparts[55,56]; and (2) the development of processes for higher alcohols production from ethanol, and their etherification reactions. These chemistries are needed for the production of higher cetane number diesel[14,57]. In terms of MFSP, there are three regions of interest. First, when $40 \leq \phi_{D,CN}^{MIN} \leq 60$, the MFSP and the yield remain constant. Second, a slight increase in MFSP, with a marginal impact on the fuel yield, is observed when $60 < \phi_{D,CN}^{MIN} \leq 69$. Finally, when $\phi_{D,CN}^{MIN} > 69$ the MFSP increases, and the fuel yield decreases as the lower bound on cetane number becomes tighter.

The results presented show how the interplay between fuel properties and processes affects the economics in diesel production biorefineries. Identifying the relevant trade-offs allows us to find strategies to improve the economics of the process without significantly impacting the fuel characteristics (e.g., reducing the density lower bound by 5%). Additionally, we show that the production of high cetane number diesel can be enabled by using Guerbet coupling and etherification[14].

*Jet fuel:* In the case of jet fuel, relaxing the constraints on density and $T_{D,5}$ does not have any impact on the economics (See SI-10). Instead, we study the role of the upper bounds on viscosity and freezing
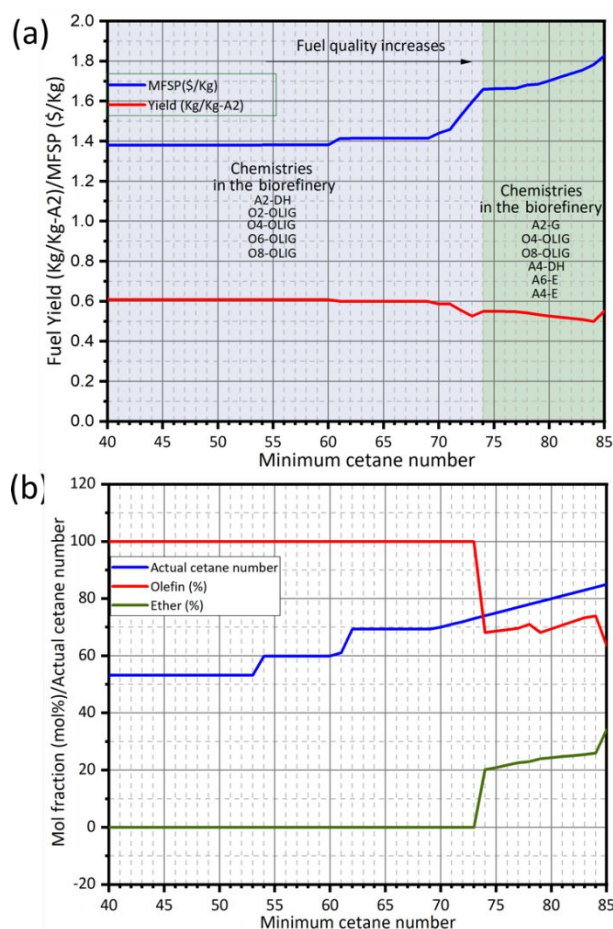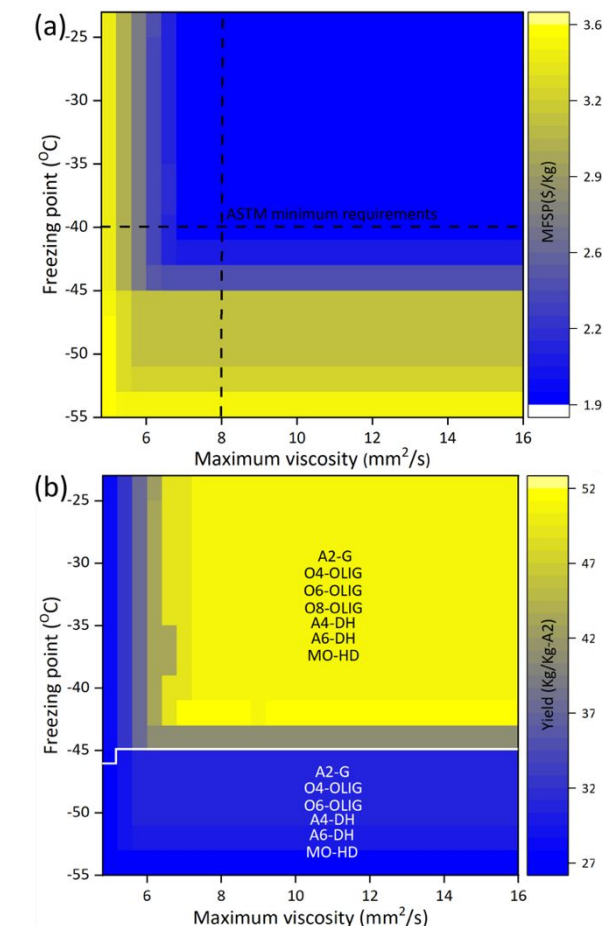
          



**Figure 6.** Effect of constraining the minimum cetane number on (a) the minimum selling price, yield, and chemistry blocks selected, and (b) the actual cetane number of the fuels produced, and the fuel composition measured as mol fraction of olefins and ethers. Density and $T_{D,5}$ are constrained based on Figure 5 results ($\rho > 780$ Kg/m$^3$ and $T_{D,5} > 150\ °C$).



Chemistry blocks are labelled such that the alphabetic characters indicate the functional group of the substrate (A: Alcohols, O: Olefins, MO: mixed olefins), and the numerical one its carbon length. The type of chemical transformation is indicated using an abbreviation (DH: dehydration, G: Guerbet coupling, OLIG: oligomerization, HD: hydrogenation).

point. The results of these investigations are shown in Figure 7. We note that, the MFSP increases when tighter constrains are enforced on both viscosity and freezing point (Figure 7(a)). Relaxing the constraints on these variables in comparison with the typical ASTM standard[44] does not improve the economics. In general, the changes in the MFSP are explained by changes in the total fuel yield **primarily effected by freezing point** (Figure 7(b)). In terms of technologies, two types of refineries are observed, both having the structure shown in Figure 3 (ethanol Guerbet coupling, higher alcohol dehydration to produce olefins, oligomerization, and hydrogenation to produce paraffins). The two types differ by the presence/absence of an octene oligomerization chemistry.

## The role of system complexity

The role of complexity, defined as the number of chemistry blocks, is studied (Figures 8-10). There is a fundamental trade-off with respect to biorefinery complexity. On the one hand, increasing complexity

**Figure 7.** Effect of constraining maximum jet fuel viscosity and freezing point on (a) the MFSP and (b) yield and chemistry blocks.

may lead to better economics. On the other hand, highly complex processes may be more challenging to operate. Consequently, understanding the relation between complexity and process economics may lead to better biorefinery designs.

Figure 8(a) shows the effect of complexity on the MFSP and fuel yield. The EE and EROI as a function biorefinery complexity are shown in Figure 8(b). In general, the EE remains approximately constant at a value between 20%-30%. In contrast, the EROI changes significantly, but a direct relation with complexity is not observed. This is because the EROI was not explicitly constrained in the model and, in some instances, a low MFSP can be obtained even if the EROI is low, that is, an energy intensive process can be profitable.

The effect of complexity on the selected chemistry blocks and catalysts is shown in Figure 9(a). Depending on the maximum number of chemistry blocks, diesel biorefineries employ three options for the initial ethanol transformation (1) dehydration, (2) simultaneous dehydration and oligomerization or (3) Guerbet coupling for the initial ethanol transformation. In all cases, a sequence of oligomerizations is used to increase the molecular weight of the components. When Guerbet coupling is selected,
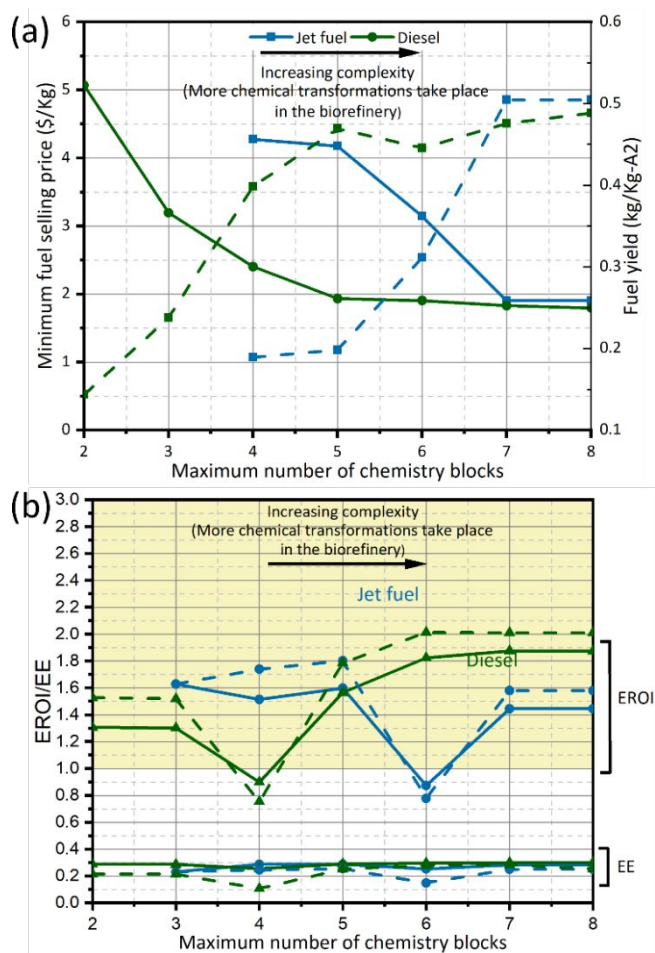
**Figure 8.** Effect of the maximum number of chemistry blocks on (a) Minimum Fuel Selling Price (MFSP) (continuous lines)) and fuel yield (Dashed lines) (b) EROI and EE in biorefineries producing jet fuel, and diesel. Dashed lines represent biorefineries in which by-products are used to partially satisfy the refinery energy needs; continuous lines represent biorefineries in which by-products are used to produce electricity that is sold to the grid. The yellow area represents the region where a net energy gain is obtained.

alcohol dehydration is used to produce olefins. In the case of jet fuel, an initial Guerbet coupling chemistry block followed by alcohol dehydration (butanol and/or hexanol) and a sequence of olefin oligomerizations is the preferred strategy. In all cases, an olefin hydrogenation chemistry block is used. We highlight that oligomerization chemistries have a prominent role in the production of middle distillates because of the need to increase the average molecular weight of the products incorporated in these fuels.

The fuel composition as a function of complexity is shown in Figure 9(b). Jet fuel consists of a blend of paraffins with more than eight carbons without oxygenated species in the blend. While diesel consists of primarily high molecular weight olefins (C10+); with a fraction of higher alcohols present in the final product when a Guerbet chemistry block is used in the refinery (4 and 5 chemistry blocks). One common feature of the chemical composition of all fuels
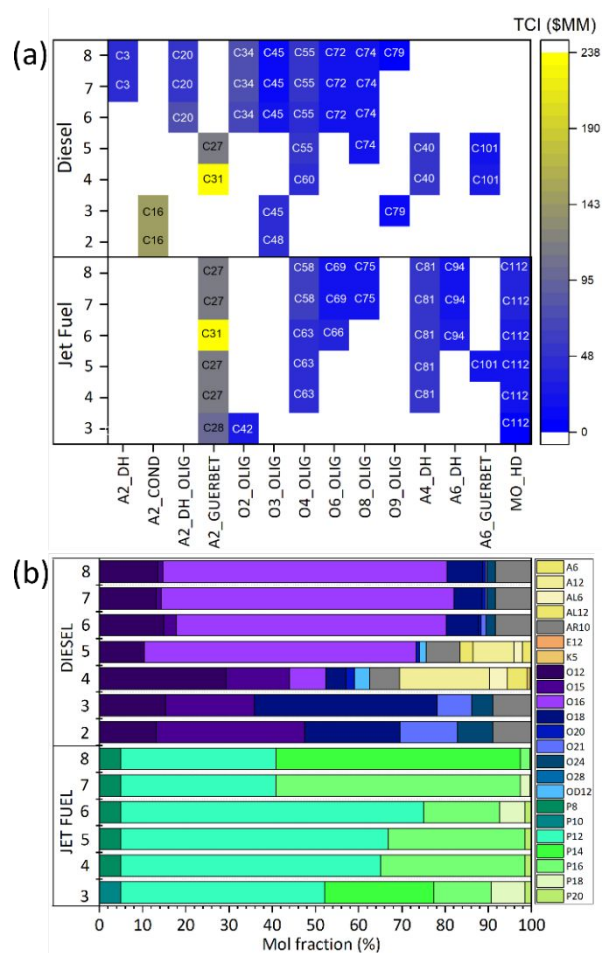


**Figure 9.** Effect of increasing the number of chemistry blocks (left axis on both panels) on (a) chemistry blocks (colored squares) and catalysts used in biorefineries. The color code indicates the level of Total Capital Investment (TCI) and the label in each square, the selected catalyst. Chemistry blocks (bottom axis) are labeled such that the first character indicates the functional group of the substrate (A: Alcohols, O: Olefins), and the second one its number of carbons. The type of chemical transformation is indicated using an abbreviation (DH: dehydration, DH+OLIG: simultaneous dehydration and oligomerization, G: Guerbet coupling, OLIG: oligomerization). (b) Fuel composition. Products are labeled using an alphabetic part to indicate the functional group (K: ketones, AL: aldehydes, ES: esters, A: alcohols, AR: aromatics, and O: olefins), and a numeric part for the number of carbons.

is their low aromatic content (<10%), which is advantageous from an environmental perspective since a high aromatic content is associated with more soot formation[58].

Finally, in Figure 10, it is shown how the fuel composition affects physical properties. Figure 10(a) shows cetane numbers, densities, viscosities, flash points, and freezing points of the fuels, after normalizing them with respect to their lower bounds. In diesel, density is the binding property (i.e., the property whose value is equal to the lower or upper bound imposed), while in jet fuel, it is the freezing point. Thus, relaxing the density specification in diesel
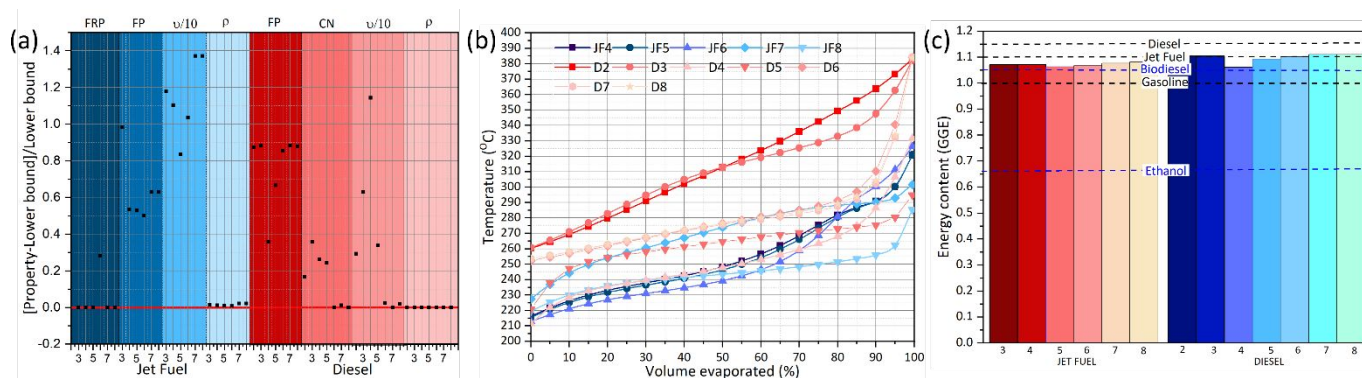
## ARTICLE



**Figure 10.** Fuel physical properties (a) Normalized values of cetane number, viscosity, and density (b) Distillation curves based on the ASTM-D86 standard. Fuels are named using an alphabetic part for the type of fuel (JF: jet fuel, and D: diesel) and a number indicating the maximum number of chemistry blocks (see legend). (c) Energy content of fuels designed. Reference energy content of fossil fuels (black dashed lines) and common biofuels (blue dashed lines) are shown.

or freezing point in jet fuels may lead to lower MFSP, corroborating our analysis in section 2. The distillation curve of each fuel based on the ASTM-D86 standard[59] using the method develop by Ferris and Rothamer[60], is shown in Figure 10(b). The fuels have physicochemical characteristics similar to those of fossil fuels. The fact that these fuels boil in a similar range to fossil fuels validates the approach that we use for the distillation curve modelling. Finally, we note that the designed fuels have lower energy content than the fossil fuels; but significantly higher than ethanol and biodiesel (Figure 10(c)).

### Emissions and fuel demand

In this section, two issues associated with biofuels research are explored. First, we analyse how much of the current and projected demand of middle distillates can be satisfied using the biofuels considered in this work. Second, we study the potential $CO_2$ mitigation of these fuels if deployed at large scale in the U.S. **We note that the presented analysis does not intend to identify the optimal allocation of biomass across different uses. It is possible that under certain assumptions other, not fuel related, biomass use may have a lower environmental impact. Also, we do not explore the indirect consequences of replacing the current uses of biomass (heating, biobased fuels, etc.)[3] with alternative technologies**.

Figure 11(a) shows the fraction of the U.S. middle distillates demand that can be satisfied if all available biomass resources, determined in the 2016-billion-ton study[61], were used to produce ethanol. Our analysis is constrained such that the ethanol demand for gasoline blending (10%) is satisfied first, the remaining ethanol is upgraded to either diesel or jet fuel. The figure shows two bands, one per fuel, their upper boundaries correspond to the most optimistic scenario, while the lower boundaries correspond to the most pessimistic scenario. In the former, biomass availability is consistent with the high yield estimates in the Billion-ton report[61], and fast and

significant improvements in ethanol production and upgrading leading to significant reductions in the energy consumption in these processes are assumed. In the later biomass availability is given by the low yield scenario in the billion-ton report[61] and negligible improvements in ethanol production and upgrading are considered. In all cases a time varying fuel demand given by EIA estimates of middle distillate consumption is used in the calculations[62] (See SI-12 for details). The potential jet fuel supply surpasses the demand in all scenarios. Conversely, for diesel, we observe that in the most optimistic scenario 100% of the demand could be satisfied by ~2035, while in the pessimistic one only a maximum of ~75% could be satisfied. For reference, current and 2050 middle distillate demands are: 2.35EJ and 4.77EJ for jet fuel; and 8.19 EJ and 8.75EJ for diesel.

In general, the $CO_2$ mitigation potential of the fuels studied herein follows the following order ethanol>diesel>jet fuel (See SI. 12). Based on these considerations, and assuming that the maximum fraction of ethanol blended with gasoline will be 10%, a biofuel production policy to minimize the total $CO_2$ emissions is determined. The fraction of the gasoline, jet fuel, and diesel demand that can be satisfied by following this policy is shown in Figure 11(b). In all scenarios 10% of the gasoline demand is satisfied. In the most optimistic scenario, all ethanol not blended with gasoline is used to produce diesel until ~2035, when 100% of the demand is satisfied. From ~2035 onwards, the ethanol produced is enough to satisfy the diesel demand and to produce jet fuel. By 2050, the fraction of the jet fuel demand that can be satisfied is >80%. In the pessimistic scenario, all ethanol not blended with gasoline is used to produce diesel and by 2050 >65% of the demand could be satisfied. The fraction of $CO_2$ emissions abated by following the optimal production policy is shown in Figure 11(c). The mitigation potential is presented both with respect to the total and the transportation sector
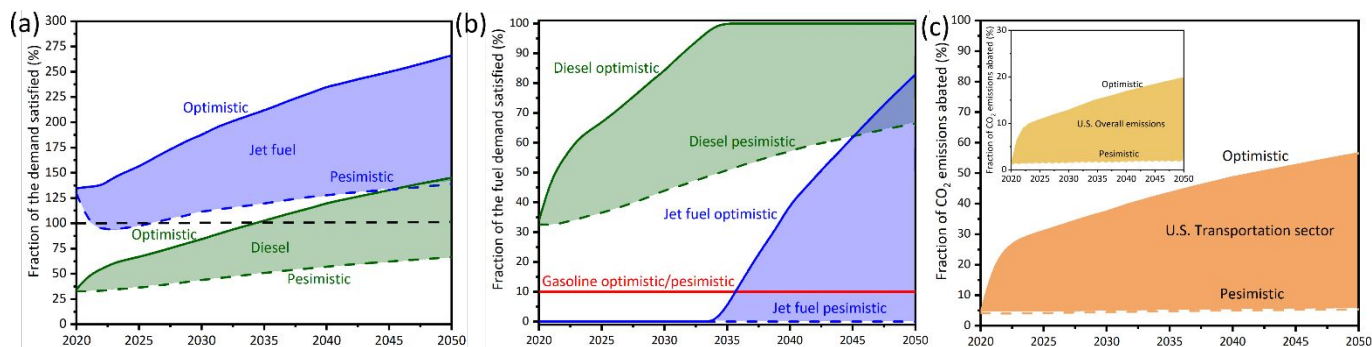
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**Figure 11.** (a) Fraction of current and forecasted jet fuel and diesel demand that could be satisfied if all U.S. available biomass is used to middle distillates via ethanol upgrading. Upper boundary in each band corresponds to an optimistic scenario in terms of biomass availability and technology advancement, while the lower boundary corresponds to a pessimistic scenario. (b) Fraction of the current and forecasted demand of each fuel that could be satisfied if a production policy that minimizes $CO_2$ emissions is implemented. (c) Potential $CO_2$ mitigation as a fraction of the U.S transportation section emissions, and the U.S overall emissions (inset).

emissions in the United States. By 2050, between ~5%-50% of the U.S. transportation emissions could be abated, which is equivalent to a ~2%-20% reduction in the national emissions. The difference between the optimistic and pessimistic scenarios is mainly by differences in the emissions associated with ethanol production. In the most optimistic case we assume that it is possible to produce carbon neutral ethanol[63], while in the most pessimistic case we rely on recent estimates that establish emissions of ~55 g-$CO_2$-eq /MJ of ethanol obtained from corn stover[64]. These results stress the importance of improving ethanol manufacturing technology and supply chain to be able to harness the sustainability potential of alternative fuels.

**The analysis presented in this work is based on U.S. data. However, these technologies may be employed in other regions of the world. Southeast Asia for example has the potential of producing between 7.1-14 EJ of biomass energy by 2050[65], which would lead to 1.8-3.6 EJ of diesel or 2.1-4.1 EJ of jet fuel based on the yields obtained in this work. In the case of Europe, the biomass production potential by 2050 is between 1.5-5.6EJ[66], which would yield 0.38-1.45EJ of diesel or 0.4-1.6 EJ of jet fuel. Estimations of biomass availability in Africa vary widely, between 2.5 and 317 EJ[67], which could yield 0.65-82EJ of diesel or 0.74-93.8 EJ of jet fuel.**

## CONCLUSIONS

A systems-level analysis of the production of middle distillates (jet fuel and diesel) from ethanol is presented based on a general framework which simultaneously considers the processing costs and properties of the fuels.

The relationships among fuel properties, selected chemistries, and MFSP were established. The understanding of these relationships was used to improve the biorefinery economics; and to identify processes to produce advanced biofuels with tailored properties (e.g., diesel with high cetane numbers).

The role of biorefinery complexity on the process economics and energetics was also established. It was shown that increasing the biorefinery complexity leads to higher yields and lower MFSP.

It was shown that if lignocellulosic ethanol is used as feedstock, an $EROI > 1$ can be obtained, with an overall energy efficiency of ~25%. Higher values are contingent upon improvements in ethanol production and upgrading.

Finally, it was shown that in the most optimistic scenario, if the total U.S. biomass resources were used to produce the fuels described in this work, it would be possible to satisfy the entire diesel demand and more than 80% of the jet fuel demand by the year 2050. In the most pessimistic case, only ~75% of the diesel demand would be satisfied. Reductions in the national $CO_2$ emissions associated with the production and use of these fuels would range between ~2%-20%.

## Author Contributions

Juan-Manuel Restrepo-Flórez: conceptualization, data curation, formal analysis, investigation, methodology, software, visualization, writing–original draft. Joonjae Ryu: conceptualization, formal analysis, investigation, methodology, software, writing –original draft. Dustin Witkowski: conceptualization, formal analysis, investigation, methodology, software, writing –original draft. David Rothamer: conceptualization, resources, funding acquisition, supervision, project administration, writing – review & editing. Christos T. Maravelias: conceptualization, methodology, resources, funding acquisition, supervision, project administration, writing – review & editing.

## Conflicts of interest

There are no conflicts to declare.

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