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Bio-oil co-processing can substantially contribute to renewable fuel production potential and meet air quality standards

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HIGHLIGHTS

- Changes in air emissions due to co-processing bio-oil in refineries are quantified.
- Most refineries can co-process ≥5% of bio-oil without requiring major air permit.
- Co-processing potential for U.S. refineries is estimated.
- Co-processing can yield 1.9 billion gallons gasoline equivalent of renewable fuel.
- Extensive modifications are not required for compliance with federal regulations.

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ABSTRACT

Co-processing raw bio-oil derived from lignocellulosic biomass in existing petroleum refineries represents a near-term greenhouse gas mitigation strategy by producing partially renewable and infrastructure-compatible hydrocarbon fuel with minimal capital requirements. One deterrent for risk-averse refinery owners is that a modification to their air permit may be required prior to any changes to refinery operations due to potential air emission changes. However, a lack of information on potential air emission changes resulting from bio-oil co-processing yields uncertainty, which could cause delay in obtaining required permit. To address this concern, we perform a quantitative evaluation of air emission changes across a range of bio-oil co-processing fractions in refineries' fluid catalytic cracking units. We find that 92% of U.S. petroleum refineries could co-process 5% or more (up to 20%, by weight) raw bio-oil without triggering major permitting requirements. We then develop an upper bound estimate of the potential for co-processing bio-oil considering permitting and technical limits; our results suggest that U.S. refineries could co-process 573,000 barrels per day (0.79 cubic meter per second) of raw bio-oil, implying ~1.92 billion gallons gasoline equivalent of renewable fuel per year (0.23 cubic meter per second), equivalent to 1.4% of U.S. gasoline consumption or 18% of ethanol production in 2018. This first-of-its-kind analysis integrates process and environmental engineering with air permitting analysis and demonstrates the importance of coupling regulatory considerations with engineering analysis to guide informed decision-making to minimize investment risks while fully leveraging refinery infrastructure. This novel approach is also applicable to refineries in other jurisdictions.

1. Introduction

Low-cost yet underutilized lignocellulosic biomass has attracted worldwide attention as a source for renewable fuels that could diversify the transportation energy supply and reduce emissions from the transportation sector. As there is an increased interest in adopting renewable energy directives and standards globally for producing and utilizing fuels with renewable content [1–3], the petroleum refinery sector has been seeking ways to comply with the directives and mandates by utilizing their existing infrastructure without significantly changing its design or operation. Biomass and its subsequent conversion to bioenergy offers an opportunity to potentially boost domestic economic growth across the supply chain, lower net greenhouse gas emissions and enable energy diversity and independence.

A recent biomass resource assessment indicates the United States has abundant low-cost biomass feedstocks, which could be used as a supplement to crude oil for renewable fuel production [4]. One option is to use raw bio-oil produced from biomass feedstock for co-processing

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with petroleum-intermediate feedstocks in refineries. This option has attracted interest from refineries for its potential to provide renewable content in transportation fuels at economically competitive prices given its low capital requirement and the fuels' compatibility with existing transport and distribution infrastructure [5–7]. Co-processing herein refers to the simultaneous transformation of biogenic feedstocks and intermediate petroleum products such as vacuum gas oil (VGO) in existing petroleum refinery process units to produce hydrocarbon fuels with partial renewable content [3,8].

Ongoing research and industrial demonstrations suggest co-processing in existing petroleum refineries' fluid catalytic cracking (FCC) units (which convert heavy molecular weight components of petroleum feeds into lighter products such as gasoline, light cycle oil, propylene, and butylene) [9–11] could be a technically feasible option to produce partially renewable hydrocarbon fuels at a commercial scale after refineries adopt the appropriate and necessary modifications [12–14]. FCC units can be adjusted to varying feeds by changing operating conditions and modifying catalysts [15]. Pinho et al. [16,17] demonstrated three different pyrolysis-derived raw bio-oil/VGO co-processing ratios: 5%/95%, 10%/90% and 20%/80% (all percentages herein are by weight unless noted otherwise) at a demonstration FCC unit of the Petrobras' refinery in São Mateus do Sul (State of Paraná, Brazil). Pinho et al. [16,17] also indicted that co-processing of raw bio-oil in FCC units is technically feasible by feeding VGO and raw bio-oil separately at different injection points in the reactor. The product yields (such as gasoline) were found to be similar to the base FCC unit feed (i.e., 100% VGO) when up to 10% raw bio-oil was co-processed; a noticeable drop in the gasoline yield was observed when 20% raw bio-oil was used. Analysis of representative samples also verified the presence of renewable carbon in gasoline and diesel products. Ibarra et al. [18,19] recently studied the effects of different zeolite-based catalyst along with varying catalyst to bio-oil ratio on the FCC product distribution for different types of raw bio-oil and concluded that optimal hydrocarbon yields can be achieved using commercial zeolite catalyst. The desire to produce renewable fuels to meet regulatory requirements has brought refineries and bio-oil producers together to investigate and pursue this opportunity (e.g., Chevron & Marathon [8], Envergent technologies by Universal Oil Products and Ensyn [20,21], and Technip & BTG Bioliquids [22]).

While previous studies have analyzed the technical and economic viability of co-processing raw bio-oil with VGO in the FCC unit(s) of a petroleum refinery, none of the studies have examined air emission changes and regulatory implications associated with implementing bio-oil co-processing in existing petroleum refineries. In the United States, the petroleum refineries must obtain the appropriate air pollutant emission permits prior to retrofitting the facilities to co-process raw bio-oil because the modifications to refinery process units and operations that are needed to co-process raw bio-oil would likely lead to changes in the refinery's "potential-to-emit" (PTE; defined as the maximum capacity of a stationary source to emit a pollutant under its physical and operational design) [23] and thus require a new source review (NSR) permit [24].

The air pollutants that trigger the need for an NSR permit are the so-called criteria air pollutants, for which the U.S. Environmental Protection Agency (EPA) has set national concentration limits, known as National Ambient Air Quality Standards (NAAQS). The criteria pollutants are particulate matter (PM), carbon monoxide (CO), sulfur oxides (SO_x), nitrogen oxides (NO_x), ozone (regulated through its precursors, NO_x and volatile organic compounds [VOCs]), and lead (Pb). Hazardous air pollutants (HAPs) are regulated by National Emission Standards for HAP (NESHAP) under the Clean Air Act (CAA) [25,26], but HAP emission increases do not trigger the need for an NSR permit.

Under the CAA, the NSR program requires an air permit when proposed modifications that cause a significant emissions increase are made to a major emitting source (i.e., "major source"). Because all petroleum refineries in the United States are major sources [27] and because the modifications required to co-process bio-oil could lead to an increase in emissions of criteria air pollutants, it is critical that refineries assess how bio-oil co-processing might affect petroleum refineries' air emissions and to understand what the implications are from an air-permitting perspective, as their continued operation depends on obtaining all required permits (refer to the supplementary information [SI] for more information).

The primary objective of this analysis is to examine how emissions would change with different levels of bio-oil co-processing, identify the changes that could trigger NSR permitting, and establish a potential of bio-oil co-processing that would keep emissions below the significance level that triggers major NSR permitting. A minor NSR permit ensures emissions from source modifications do not violate local air pollution control strategies, entails a simpler application, can be issued more quickly, and imposes no new emission control requirements. For the United States case study, we use two criteria to achieve the objective of avoiding major NSR requirements and estimating the potential of raw bio-oil co-processing: (1) restricting co-processing to a level such that the emission increase of a pollutant would not trigger the requirement for a major modification permit under the prevention of significant deterioration (PSD) or nonattainment new source review (NNSR) and (2) constraining raw bio-oil co-processing to 20% as a technical upper bound [16,28,29]. Another objective of this analysis is to determine whether the process modifications at the petroleum refineries would trigger additional air pollution regulations. We evaluate the applicability of relevant new source performance standards (NSPS) and NESHAP rules and consider how the locations of petroleum refineries and the varying processing capacity of the FCC units may lead to different levels of NSR permitting requirements (i.e., major versus minor modification permit). However, given that our regulatory analysis focuses only on the U.S. federal rules, the regulatory and permitting implications drawn from this analysis are only appropriate for screening-level assessment. Any refinery-specific permit application should also consider the potential applicability of state or local air regulations.

Findings from this analysis could help refinery owners make informed decisions by reducing uncertainties related to air permitting and air regulatory requirements for bio-oil co-processing. While our quantitative analysis focuses on the refineries in the United States, the novel approach developed in this analysis could be applied to refineries in other jurisdictions, and this paper demonstrates the importance of considering regulatory requirements within engineering analysis to help guide informed decision-making. It is important to note that our analysis neither addresses the capital and operation cost requirements for co-processing nor evaluates how co-processing could reduce the lifecycle greenhouse gas intensity of the produced fuels, although these factors will influence investment decisions.

2. Methodology

2.1. Fluid catalytic cracking unit capacities

To co-process raw bio-oil, a petroleum refinery should be able to convert bio-oil into fuel products, which is generally achieved by FCC and/or hydrotreating/hydrocracking [30]. Recent pilot- and demonstration-scale experiments and studies conducted on FCC units have demonstrated the feasibility of co-processing up to 20% of raw bio-oil (also known as pyrolysis bio-oil or py-oil) with VGO in existing refineries' FCC units [16,28,29]. However, processing chemically different bio-based intermediates in FCC units is still a new concept for refineries. The refineries need to have sufficient confidence to ensure co-processing raw bio-oil does not pose additional risks that jeopardize the safety, reliability, predictability, or profitability of their normal operations [30]. A previous study indicates that a 5% bio-oil co-processing rate for a typical commercial FCC unit is considered a reasonable starting point [17]. Therefore, our first step is to estimate potential changes in air pollutant emissions resulting from a 5% raw bio-oil co-processing with VGO in FCCs. Then, we scale emissions for higher co-processing rates (up to 20%) except for emissions associated with equipment leaks from additional piping and pumping, which are discussed in detail in Section 2.2.2.

An assessment conducted by the Pacific Northwest National Laboratory (PNNL) [30] categorized refineries in the United States based on the flexibility of bio-oil co-processing capability, which is typically achieved through FCC, hydrotreating, or hydrocracking units in the refinery. Research to date has demonstrated successful co-processing of raw bio-oil with VGO in FCC units. So, our analysis focuses exclusively on co-processing raw bio-oil in refineries' FCCs. Using data on petroleum refineries in the United States from the U.S. Energy Information Administration (EIA), we identified the refineries that are equipped with FCC units [31]. Of the 124 refineries listed in the EIA database, 95 have FCC units with feed capacities ranging from 2900–232,500 barrels (bbl) of VGO per calendar day (0.004–0.32 cubic meter per second [m^3/sec]). At a 5% co-processing rate, this FCC capacity range of existing petroleum refineries corresponds to a bio-oil co-processing capacity of 115–9200 bbl/day (0.0002–0.013 m^3/sec) for an individual refinery equipped with FCC units (assume a raw bio-oil density of 1200 kg per m^3 [kg/m^3] [32,33,34], which is equivalent to 75 lb per cubic feet [lb/ft^3]).

We group the FCC-equipped petroleum refineries into three size categories, 0–27,850 bbl/day (0–0.04 m^3/sec), 27,850–68,350 bbl/day (0.04–0.09 m^3/sec), and 68,350–232,500 bbl/day (0.09–0.32 m^3/sec), with each category having an approximately equal number of refineries, to estimate the corresponding bio-oil co-processing capacity at a 5% co-processing rate (refer to Table 1). The first size category of refineries in the United States includes 32 refineries with FCC units, which can process up to 1,100 bbl/day (0.0015 m^3/sec) of raw bio-oil. The second and third size categories of refineries can co-process up to 2700 and 9200 bbl/day (0.004 and 0.013 m^3/sec) of raw bio-oil, respectively.

2.2. Estimation of potential increase in petroleum refinery emissions

2.2.1. Determining process modifications

Two thermochemical process pathways can feasibly be used to produce raw bio-oil: fast pyrolysis [35] and hydrothermal liquefaction [36]. For this analysis, we assume the raw bio-oil is produced via a commercially established fast pyrolysis process pathway such as the one developed by Honeywell UOP and Ensyn [37]. The raw bio-oil would then be used for co-processing with VGO in the FCC units. Raw bio-oil is assumed to be shipped to the petroleum refinery by fuel tank trucks. To ensure proper implementation of bio-oil co-processing in the FCC units, several process modifications are required at the petroleum refineries. Based on research from previous co-processing tests and studies [6,17,38,39] as well as our engineering judgement, the following four important changes to the unit processes and operations are needed to co-process raw bio-oil in the FCC units at petroleum refineries, in addition to material changes (e.g., amount of FCC catalyst).

(1) Delivering raw bio-oil to petroleum refineries by fuel tanks
(2) Adding a new liquid storage system for raw bio-oil
(3) Installing associated piping and pumping equipment to transfer raw bio-oil from the tank or tanks to the FCC units
(4) Adding a new feed system dedicated to injecting raw bio-oil into the riser reactor. Note that raw bio-oil and VGO are injected at two different points to increase thermal cracking and avoid undesirable reactions.

Fig. 1 illustrates the modifications to the process and operations, which are necessary for co-processing raw bio-oil with VGO in the FCC units.

2.2.2. Estimating increase in potential-to-emit of criteria air pollutants and greenhouse gas emissions

Once we have identified the physical and operational changes required for the petroleum refinery, we use emissions factors from the AP-42 database [40], EPA documents, source-specific models, and experimental data from published literature to quantify the PTE of criteria pollutant emissions resulting from these changes, assuming continuous operations 365 days a year (refer to PTE definition in the Introduction Section). These emission factors and tools are commonly used by regulatory agencies to estimate PTE for permitting purpose. In addition, co-processing bio-oil with VGO leads to redistribution of products from the FCC (i.e., changes in the yields of products such as gasoline, light cycle oil, dry gas, and bottoms) compared to processing pure VGO [41]. The resulting changes in emissions of regulated pollutants are also considered in this analysis. However, we do not estimate changes in HAP emissions as they are not regulated under the NSR permitting program. Below we describe the methods used to estimate emissions associated with each change listed in Section 2.2.1

(1) PM, PM_{10} and $PM_{2.5}$ Emissions from Tank Trucks Delivering Bio-Oil to Refineries

Additional truck traffic resulting from the delivery of raw bio-oil by fuel tank trucks is expected to generate emissions of PM, PM_{10} (PM with diameter less than or equal to 10 μm), and $PM_{2.5}$ (PM with diameter less than or equal to 2.5 μm). We assume all the truck traffic would be on unpaved roads, and the round-trip distance is 0.25 miles (402 m) within the petroleum refinery's boundaries. The average tank truck is assumed to weigh 32 tons (29,030 kg) and hold up to 152 bbl (24.17 m^3) of bio-oil. The EPA's AP-42 method for calculating fugitive dust emissions (PM, PM_{10}, and $PM_{2.5}$) from unpaved roads [42] is used to estimate emissions from truck traffic (Eq. (1)).

$$E_{unpaved\_road} = k * \left(\frac{sC}{12}\right)^a * \left(\frac{W}{3}\right)^b * \left(1 - \frac{P}{365}\right) \tag{1}$$

Where:

$E_{unpaved\_road}$ = annual emissions from unpaved roads per vehicle mile traveled (lb/vehicle mile traveled; to convert lb/vehicle miles traveled to kg/vehicle meters traveled, multiply by 0.00028).
k, a, b = constants (varying by specific particle size range; see Table 13.2.2-2 for Industrial Roads in EPA [42])
sC = silt content of unpaved road surface (%)
W = average weight of the vehicles traveling the roads (tons)
P = number of days per year with at least 0.01 in. (0.000254 m) of precipitation (days/year) (default = 90)

Table 1
Bio-oil volumes for 5% co-processing in petroleum refineries' FCC units by three size categories.

Size category	FCC capacity (barrels per day)	Bio-oil volume (barrels of raw bio-oil per day)	Number of refineries
1st	≤27,850	≤1,100	32
2nd	>27,850 and ≤ 68,350	>1100 and ≤ 2700	31
3rd	>68,350 and ≤ 232,500	>2700 and ≤ 9200	32

1 barrel per day = 1.38E−06 m^3/sec.

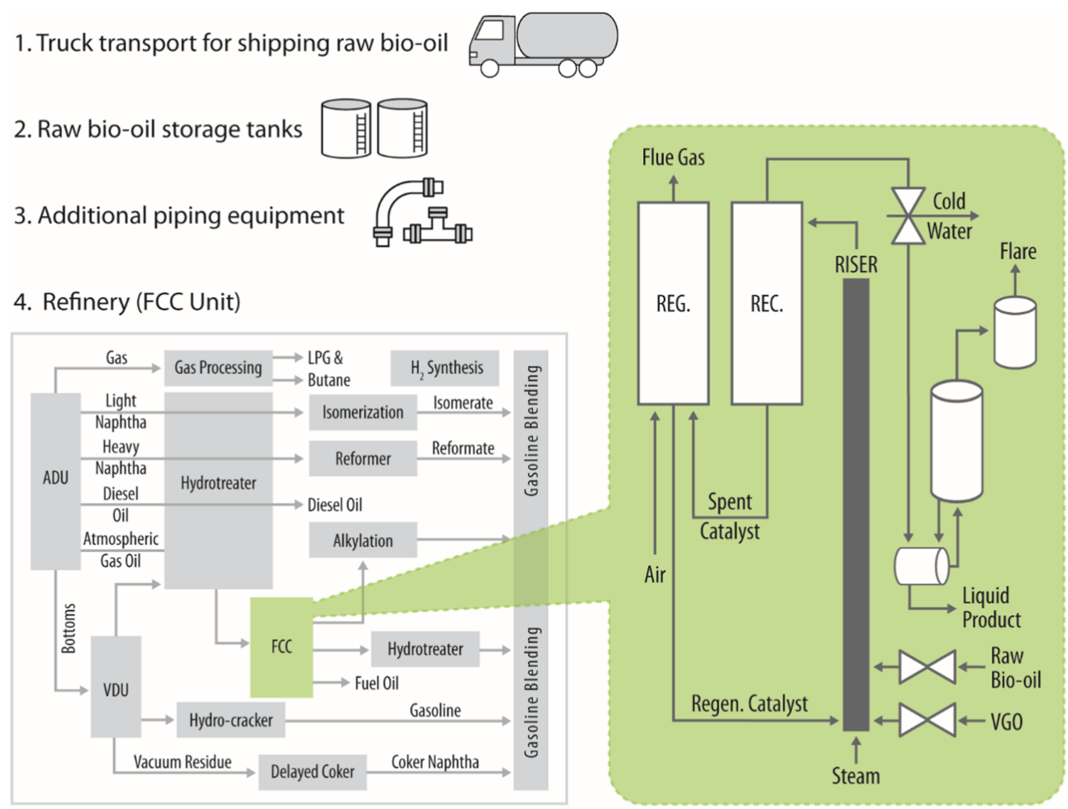

Fig. 1. Modifications to petroleum refinery unit operations needed to co-process raw bio-oil in FCCs (adopted from Pinho et al. [16,17]). LPG = liquified petroleum gas, ADU = atmospheric distillation unit, VDU = vacuum distillation unit, FCC = fluid catalytic cracking unit, H_2 = hydrogen, REG = regenerator, and REC = reactor.

The number of tank trucks entering and leaving the petroleum refinery is based on the raw bio-oil requirement at a 5% co-processing rate, which varies by refinery.

(2) VOC Emissions from Newly Added Storage Tanks

The new bio-oil storage tank or tanks are expected to result in additional VOC emissions. Three sources of VOC emissions associated with the storage tanks are considered: evaporative losses during storage (breathing losses or standing storage losses), evaporative losses during loading operations (working losses) and flashing losses. The EPA's TANKS program [43], which was designed to estimate emissions from these sources, is used in our analysis.

Vapor pressure and molecular weight are important characteristics of a material that impact storage tank emissions. The molecular weight of raw bio-oil is estimated to be 500 Daltons (0.5 kg/mol), which is similar to heavy VGO (0.463 kg/mol) while the vapor pressure is assumed to be 5 kPa (kPa) at 38 °C (311 K) [44,45]. Raw bio-oil is assumed to be stored onsite in a fixed-roof storage tank, whose construction typically costs half of that for a floating roof tank [46]. We estimate the emissions from the raw bio-oil storage tank(s) for a petroleum refinery located in Houston, Texas, because of the high concentration of refineries in that area. The storage tank is sized for a 14-day bio-oil storage capacity. For petroleum refineries that can co-process up to 1100 bbl/day of bio-oil (the first size category), a storage tank with a capacity of 700,000 gallons (2650 m^3) is sufficient for 14-day bio-oil storage. The second size category of petroleum refineries (i.e., those co-processing up to 2700 bbl/day [0.004 m^3/sec]) can install a storage tank with a capacity of 1.5 million gallons (5679 m^3), and the third size category (i.e., those co-processing up to 9200 bbl/day [0.013 m^3/sec]) can install one with a capacity of 5.5 million gallons (20,820 m^3). All these parameters are used as inputs to the TANKS model to estimate VOC emissions.

It is important to note that information on raw bio-oil's vapor pressure is scarce. The vapor pressure assumed for raw bio-oil is based on data obtained from one material safety data sheet [39], a project report from a company characterizing raw bio-oils [40], and an estimate made using a latent heat of vaporization value of 609,900 J/kg [47] in the Clausius-Clapeyron equation [48]. The physio-chemical properties of raw bio-oil would vary depending on the chemical characterization, conversion conditions, type of feedstock and water content in the bio-oil [49]. The vapor pressure used in this analysis appears to be much higher than that of VGO, which has a vapor pressure of about 2.8 kPa at 38 °C (311 K). We assume a relatively high vapor pressure for the raw bio-oil, which could lead to overestimating VOCs from storage tanks. However, from an air-permitting application perspective, the PTE [50] estimation typically requires assuming upper-bound values, especially for new chemicals, whose physical and chemical properties may vary considerably. Based on these estimates and assumptions, we use the TANKS 4.09D model for a vertical fixed-roof tank to estimate the VOC emissions. Improving estimates of physio-chemical properties of bio-oil is noted as an area for future research.

(3) VOC Emissions from Associated Piping and Pumping System

The additional piping and pumping system needed for transferring bio-oil from the storage tank or tanks to the FCC units is expected to generate fugitive VOC emissions, which are vapor or liquid leaks from fittings on various equipment (e.g., pumps, valves, and connectors). Emissions from leaking equipment are estimated based on the emission factors from the EPA's Protocol for Leak Emission Estimates [51]. We use the emission factors for synthetic organic chemical manufacturing industry (SOCMI) equipment in light liquid service because bio-oil is expected to be a light liquid. Moreover, using light liquid service emission factors also provides a more conservative estimate, which would avoid underestimating emissions for permit applications. The number of additional equipment components (e.g., pumps, valves, and connectors) needed for co-processing is determined by the number of FCC units and the length of piping needed from the storage tanks to the FCC unit based on engineering judgement [51]. It was assumed that a refinery that can co-process up to 1100, 2700, and 9200 bbl/day (0.0015, 0.004, and 0.013 m^3/sec) of raw bio-oil would have one, two, and four FCC units, respectively. For each FCC unit, the following component counts were used: 4 valves, 4 pumps, 2 pressure-relief valves, 2 sampling connections, and 20 connectors.

(4) Emissions from New Dedicated Feed System for Bio-Oil

Adding a new feed to the riser for bio-oil injection is not likely to increase emissions. This is because the characteristics (e.g., vapor pressure) of raw bio-oil are similar to those of VGO and are not expected to cause a change in the quantity or type of emissions, especially given that the feed capacity of FCCs remains unchanged. Because raw bio-oil contains lower concentrations of some precursors (e.g., sulfur and chlorine) that lead to the generation of many of the regulated pollutants, it is possible the emissions of some regulated pollutants might decrease. However, the chemical and physical compositions of raw bio-oils depend on many factors, such as conversion conditions and feedstock types. As the information on the properties of bio-oil that could be used in a specific petroleum refinery is unavailable, we do not consider any emission reduction that could result from potential replacement of VGO with raw bio-oil in PTE calculations.

(5) Emissions of Carbon Monoxide (CO) and Carbon Dioxide (CO_2) from FCC

Because bio-oil contains oxygen, oxygenated compounds including CO, CO_2, and water are formed during co-processing of raw bio-oil with VGO in FCC. In comparison, cracking pure VGO does not produce CO, CO_2 or water, though some CO and CO_2 formed in the regenerator can be observed in the products due to their entrainment in the regenerated catalyst [16]. The flue gas from FCC then passes through a high-temperature FCC catalyst regenerator and a CO waste heat boiler, where almost all the CO is converted to CO_2. We estimate the potential increase in CO emissions based on CO yield (defined as the ratio of CO mass in the FCC products to the total mass of the feed to FCC) from Pinho et al. [17], and we assume 99% of CO emissions would be reduced [52]. Similarly, the potential increase in CO_2 emissions is estimated based on CO_2 yield from Pinho et al. [17] and the CO_2 converted from CO downstream of the FCC unit.

2.3. Determining the permitting implications

To determine whether the modifications needed to co-process raw bio-oil would be subject to major modification permitting requirements [26], we compare the estimated increase in PTE with the major source modification threshold (Table 2) for each criteria pollutant that is expected to be emitted as the result of the changes made to a refinery. If the estimated emission increase of any one of the NSR-regulated pollutants equals or exceeds its applicable major source modification threshold, the appropriate major permitting requirements (either PSD or NNSR) are triggered for each such pollutant, depending on whether the refinery is located in an attainment area (PSD) or non-attainment area (NNSR) for the pollutant. Refer to the SI for detailed information on pollutants regulated under the NSR program, type of air permitting requirements, and U.S. federal rules that apply due to the modifications at an existing facility.

Facility construction and modification became subject to PSD permitting for greenhouse gas (in terms of CO_{2e}) emissions in 2011. Under current PSD regulations, however, the requirement to obtain an NSR permit is not triggered based on GHG emissions alone. The construction or modification of a source is subject to permitting for GHGs only if the construction or modification is already subject to PSD review for a non-GHG pollutant and also has the potential to emit 75,000 tons per year (tpy) (2.16 kg/sec) or more of GHGs. At one time, the PSD rules specified conditions for permitting based on GHG emissions alone, but those provisions were vacated by the U.S. courts and no longer apply (Table 2).

If the estimated increase in PTE of a regulated pollutant equals or exceeds the major source modification threshold, we use the Reasonably Available Control Technology (RACT)/Best Available Control Technology (BACT)/Lowest Achievable Emission Rate (LAER) Clearinghouse database [53] to identify emission control options that a petroleum refinery could choose to install to reduce emissions. If the control technologies are available to reduce the estimated emission increase to below major source modification thresholds, we take an additional step to explain how the refineries could avoid triggering the major modification permitting requirement.

Table 2
PSD and NNSR major modification thresholds.

Pollutants	PSD Significant Emission Rate for Attainment Areas (tons per year)	Nonattainment Area Classification	NNSR Significant Emission Rate for Nonattainment areas (tons per year)
PM	25	n/a	n/a
PM_{10}	15	Serious, Moderate	15
$PM_{2.5}$	10	Serious, Moderate	10
Ozone (regulated through its precursors, i.e., VOC and NO_x)	40 (VOC or NO_x)	Moderate, Marginal	40
		Severe, Serious	25
		Extreme	Any increase in actual emissions
CO	100	Serious	50
SO_2	40	Nonattainment	40
Pb	0.6	Nonattainment	0.6
GHG (in terms of CO_{2e})	75,000*	n/a	

NSR = new source review, NNSR = nonattainment NSR, n/a = not applicable, PM = particulate matter, PM_{10} = particulate matter with diameter less than or equal to 10 µm, $PM_{2.5}$ = particulate matter with diameter less than or equal to 2.5 µm, VOC = volatile organic compounds, NO_x = nitrogen oxides, CO = carbon monoxide, SO_2 = sulfur dioxide, Pb = lead, GHG = greenhouse gas, and CO_2e = carbon dioxide equivalent, 1 ton per year = 2.88E−05 kg/sec.

* The PSD significance rate for GHG applies only if a new source or the modification to an exisitng major source is already subject to permitting based on emissions from at least one other pollutant in this table.

2.4. Determining applicability of NSPS and NESHAP

Two types of U.S. federal standards regulate air pollutants from industrial plants: NSPS and NESHAP. The complete set of the NSPS is codified in Title 40, Part 60 of the Code of Federal Regulations (CFR). The complete set of the NESHAP is codified in Title 40, Parts 61 and 63 of the CFR. NSPS and NESHAP can apply to a facility as a whole or to a portion of the facility (e.g., some federal standards only apply to a specific piece of equipment at the facility).

We review the applicability criteria of each potentially applicable U.S. federal standard (NSPS and NESHAP) to determine whether any physical or operational changes made to co-process raw bio-oil would be subject to the rule. If any rule requires the installation of emission controls to achieve compliance, we consider the emission reduction in calculating our PTE estimates.

2.5. Determine raw bio-oil co-processing potential

Because the magnitude of potential emission increases resulting from the required modifications to co-process raw bio-oil varies by FCC unit capacity, co-processing rate and location of facilities (which affects emissions from bio-oil storage tanks), we use the applicable NSR major source modification thresholds along with a technical upper limit for raw bio-oil co-processing in FCCs without causing significant deterioration to FCC performance as two criteria to estimate the bio-oil co-processing potential for refineries equipped with FCC in the United States. We assume a petroleum refinery would co-process as much bio-oil as its FCC capacity allows without triggering the requirement for a major modification permit under PSD or NNSR due to emission increase of any pollutant or exceeding the upper bound of 20% raw bio-oil co-processing rate. We choose a 20% raw bio-oil co-processing rate as our upper limit based on findings from a number of lab-, pilot- and demonstration-scale tests [12,15,16,28,29], which have observed a notable decrease in the gasoline and light cycle oil yields caused by the high water content in raw bio-oil. In addition to product yields, co-processing raw bio-oil in excess of 20% has also shown an increase in coke formation affecting catalyst selectivity, leading to increase in temperatures resulting in catalyst degradation, among other undesirable effects [16,54]. In particular, we take the following steps to estimate the co-processing rate for each petroleum refinery equipped with FCC(s). Note that CO_2 alone does not drive major modification requirement:

(1) Estimate the co-processing rate at which the VOC emission increase is equal to the applicable NSR or NNSR major modification threshold for the pollutant (refer to Table 2)
(2) Estimate the co-processing rate at which the increase in emissions of various fractions of PM emissions is equal to the applicable major modification threshold for the pollutant (refer to Table 2)
(3) Estimate the co-processing rate at which the CO emission increase is equal to the applicable NSR major modification threshold (note that no area is currently designated as nonattainment for CO NAAQS in the United States)
(4) Assume 20% as the technical upper bound for the bio-oil co-processing rate
(5) Use the lowest value determined from the first four steps as the upper-bound co-processing rate a petroleum refinery could adopt without triggering the need to apply for a PSD and/or NNSR permit, while considering the technical constraint of bio-oil co-processing in FCC units.

3. Results and discussion

Based on the physical and operational modifications required to implement raw bio-oil co-processing with VGO in FCC units (described in Section 2.2.1), the NSR-regulated air pollutants that are expected to be emitted are VOC emissions, various size fractions of particulate matter (PM, PM_{10}, and $PM_{2.5}$), and CO and CO_2 emissions. The VOC emissions would be emitted from newly installed bio-oil storage tanks and from the associated piping and pumping equipment that distributes bio-oil from the storage tanks to the FCC units. The PM would be emitted as a result of increased traffic on roads within the refinery due to shipping of bio-oil by tank trucks. Changes in CO and CO_2 emissions occur as a result of co-processing raw bio-oil, which leads to the redistribution of products from FCC units.

3.1. Estimated increases in PTE due to modifications to co-process raw bio-oil

The estimated increases in PTE of PM, PM_{10}, $PM_{2.5}$, VOC, and CO emissions for co-processing 5% raw bio-oil are shown in Fig. 2 for refineries within the three FCC size categories we analyzed. We do not show an increase in PTE of GHG (CO_{2e}) emissions, as GHG alone does not trigger major modification requirements (see Section 2.3). Refer to the SI for detailed emission estimates from each physical and operational change listed in Section 2.2.

Our results suggest that the estimated increases in PTE for PM, PM_{10}, and $PM_{2.5}$ (owing to additional truck traffic for shipping bio-oil) would be no greater than 22.0, 6.0 and 0.6 tpy (6.3E − 04, 1.7E − 04, and 1.7E − 05 kg/sec) respectively; these estimates are below the respective major modification thresholds (i.e., 25, 15 and 10 tpy [7.2E − 04, 4.3E − 04, and 2.9E − 04 kg/sec]). It should be noted that the estimated increases in PTE for PM, PM_{10} and $PM_{2.5}$ are considered conservative because we assume fuel tanks delivering bio-oil would travel on unpaved roads instead of paved roads within the petroleum refineries.

The estimated increase in VOC emissions that are due to the addition of new bio-oil storage tanks is expected not to be greater than 7.1 tpy (2.0E-04 kg/sec) for petroleum refineries equipped with FCCs processing ≤ 27,850 bbl/day (0.04 m^3/sec) of total feed (VGO + bio-oil), which could co-process up to 1100 bbl/day (0.0015 m^3/sec) of bio-oil at a 5% bio-oil co-processing rate. When co-processing up to 2700 bbl/day (0.004 m^3/sec) of bio-oil in FCC units in the refineries capable of processing ≤ 68,350 bbl/day (0.09 m^3/sec) of feed, VOC emissions could increase up to 15 tpy (4.3E − 04 kg/sec). For refineries co-processing up to 9200 bbl/day (0.013 m^3/sec) of bio-oil, up to 43 tpy (1.2E − 03 kg/sec) of additional VOC emissions could be emitted from the storage tanks and equipment leaks combined. It should be noted that the magnitude of the estimated VOC emissions depends on several key parameters, including the vapor pressure of raw bio-oil and ambient average temperature where the refinery is located. As discussed in Section 2.2.2, we use a conservatively high vapor pressure value of raw bio-oil in our calculations to ensure we do not underestimate the increase in PTE for VOC emissions. Similarly, we assume the refinery modeled in the TANKS program is located in Houston, Texas, which has a higher average ambient temperature than many other sites, where existing petroleum refineries are located. Preliminary results from a more site-specific analysis are discussed in Section 3.4.

When 5% of bio-oil is co-processed with 95% of VGO in FCC units, the largest refinery co-processing 9,200 bbl/day (0.013 m^3/sec) of bio-oil could emit up to 0.9 ton of additional CO emissions per year (2.6E − 05 kg/sec), which is significantly below both the PSD major source modification threshold of 100 tpy and the nonattainment threshold of 50 tpy (1.4E − 03 kg/sec). Because no area is currently designated as CO nonattainment in the United States, the 50-tpy threshold in Table 2 would not apply. Similarly, up to 14,500 tpy (0.42 kg/sec) of additional CO_2 are estimated to be emitted from the largest refinery when co-processing 5% raw bio-oil with VGO. The estimated increase in PTE of CO_2 emissions is below the 75,000 tpy (2.16 kg/sec) threshold.

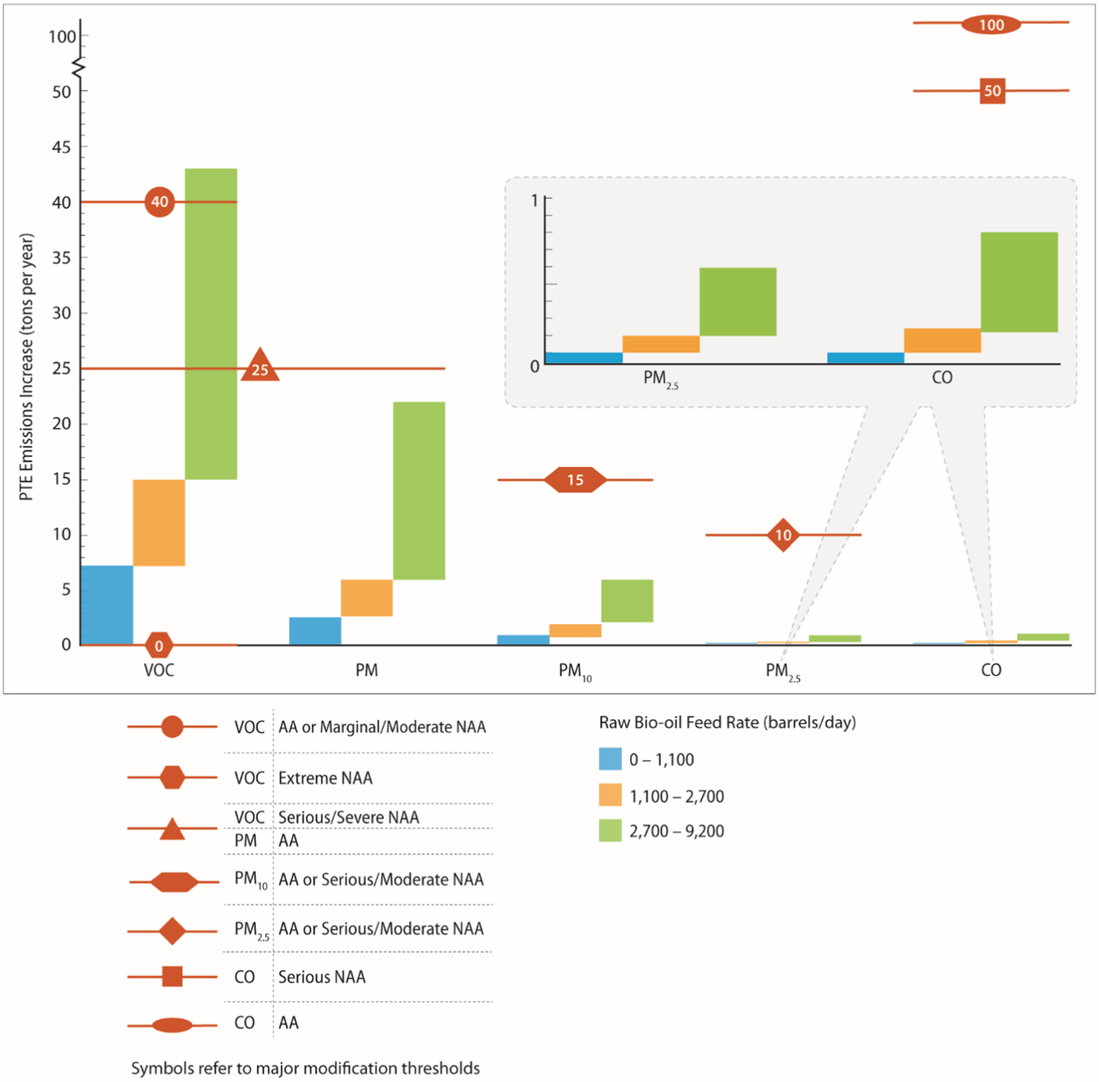

Fig. 2. Estimated increase in potential to emit for refineries to co-process raw bio-oil in fluid catalytic cracking units at the specified rates (bbl/day), represented by blue, yellow, and green colors. The numbers inside the symbols represent major modification threshold rates. Increase in emissions from petroleum refineries for co-processing 5% of raw bio-oil at the rate corresponding to three size categories in FCC units of a petroleum refinery. The figure shows major modification thresholds for the criteria air pollutants located in attainment and nonattainment areas. PTE = potential-to-emit, VOC = volatile organic compounds, CO = carbon monoxide, PM = particulate matter, PM_{10} = PM with diameter less than or equal to 10 micrometers, $PM_{2.5}$ = PM with diameter less than or equal to 2.5 micrometers, AA = attainment, NAA = nonattainment, 1 ton per year = 2.88E−05 kg/sec.

3.2. Permitting implications

3.2.1. New source review (NSR) permitting

The co-processing of raw bio-oil at a petroleum refinery will trigger the need to apply for and obtain an NSR permit before commencing construction on any modifications [24,55,56]. As described in Section 2.3, if the estimated PTE increase for each and every NSR-regulated pollutant that is expected to be emitted is lower than its applicable major modification threshold (Table 2), a minor modification permit would be required. If the estimated PTE increase equals or exceeds the major modification threshold for any one of the NSR-regulated pollutants, a PSD or major NNSR modification permit would be required, depending on the attainment status of the area where the refinery is located.

There are 95 petroleum refineries with FCC units in the United States, and 36 of them are located in a nonattainment area (NAA) for ozone and/or $PM_{2.5}$ (1997, 2006, and 2012-standard), and/or PM_{10} (1987-standard) [57]. Of these 36 refineries, 35 refineries are in an NAA for ozone, 15 for $PM_{2.5,}$ and 2 for PM_{10} (note that some refineries are located in an NAA for more than one pollutant; so, the sum of refineries in either ozone or $PM_{2.5}$ or PM_{10} NAAs exceeds 36). To co-process raw bio-oil in the FCC units of the petroleum refineries in NAAs, the refineries may need to comply with more-stringent permitting requirements and any applicable state or local emission limits [58].

For all three size categories of petroleum refineries, which could co-process up to 9200 bbl/day of raw bio-oil at a 5% co-processing rate, our results indicate that none of the petroleum refineries would exceed the major modification thresholds for PM, PM_{10} or $PM_{2.5}$ even under a worst-case scenario that assumes unpaved roads for tanks trucks transporting raw bio-oil within the refinery. Therefore, a PSD or major NNSR modification permit would not be required because of the estimated PTE increases in PM (and fractions of PM) emissions even if the refineries were located in NAAs for the $PM_{2.5}$ and PM_{10} NAAQS.

When co-processing no more than 2700 bbl/day (0.004 m^3/sec) of raw bio-oil at petroleum refineries (up to 68,350 bbl/day [0.09 m^3/sec] of FCC capacity), the estimated PTE increase in VOC emissions is expected to be less than or equal to 15 tpy (4.3E−04 kg/sec). Thus, the emissions are below the threshold for ozone attainment areas and marginal and moderate ozone NAAs (40 tpy [1.1E − 03 kg/sec]) as well as below the threshold for severe and serious ozone NAAs (25 tpy [7.2E − 04 kg/sec]). These results suggest that co-processing 5% of raw bio-oil is not expected to trigger the requirement for a major modification permit (PSD or NNSR) if the refinery is located in an ozone attainment area or in a marginal or moderate ozone NAA (all with a threshold of 40 tpy [1.1E − 03 kg/sec]) as well as in a severe or serious ozone NAA (with a threshold of 25 tpy [7.2E − 04 kg/sec]).

However, for some of the petroleum refineries with FCC capacity >68,350 and ≤232,500 bbl/day (>0.09 and ≤0.32 m^3/sec), the estimated PTE increase in VOC emissions (up to 43 tpy [1.2E − 03 kg/sec], shown in Fig. 2) could exceed the 40 tpy (1.1E − 03 kg/sec) threshold for ozone attainment areas and marginal and moderate ozone NAAs or the 25 tpy (7.2E − 04 kg/sec) threshold for severe and serious ozone NAAs. Our analysis indicates that co-processing greater than 8400 bbl/day (0.012 m^3/sec) of raw bio-oil would lead to the VOC increase exceeding the 40 tpy (1.1E − 03 kg/sec) threshold for refineries located in ozone attainment or moderate/marginal NAAs, while co-processing more than 3400 bbl/day (0.005 m^3/sec) of raw bio-oil would cause the VOC increase to exceed the 25 tpy (7.2E − 04 kg/sec) major modification threshold in a serious or severe ozone NAA. A review of EIA's refinery database and EPA's NAAQS designation and classification for ozone NAAs suggests that none of the 95 petroleum refineries equipped with FCC units is located in severe or serious ozone NAA. However, based on EIA's refinery database and EPA's air quality designations for ozone [57], six petroleum refineries in California are located in areas classified as "extreme" ozone NAA within the South Coast Air Basin. For these refineries located in extreme ozone NAAs, the NNSR major modification threshold for this classification is "any increase in actual emissions" (Table 2) [59]. Thus, co-processing of raw bio-oil at these six refineries would be subject to NNSR permitting requirements.

We evaluated emission control technologies that could be adopted to reduce VOC emissions to below the SER for all refineries except for those located in extreme ozone NAAs. One feasible option for doing this could include installing a floating roof on the fixed-roof tank [60]. A portion of the additional costs of a floating roof tank could be offset by the cost savings from product recovery achieved by suppressing raw bio-oil evaporation. Another option is to route the emissions from the storage tank(s) to a control device (e.g., thermal incinerator, catalytic incinerator, scrubber, or flare) [61–64]. Storage tank controls (either a floating roof or add-on control) would typically reduce VOC emissions by 60–99% [60]. At a minimum of 60% emission reduction efficiency, the VOC emission increase could be reduced to 17.2 tpy (4.9E − 04 kg/sec) (i.e., to below the 40 tpy [1.1E − 03 kg/sec] and 25 tpy [7.2E − 04 kg/sec] thresholds discussed above).

Although CO is a regulated pollutant under the NSR program, our estimates indicate that increases in PTE for CO are not large enough to drive the major modification permitting requirement for petroleum refineries. Concerning the increases in CO_2 emissions, PSD does not apply to CO_2 (GHGs) unless a modification is already subject to PSD review for a non-GHG pollutant and has a PTE of 75,000 tpy or more of GHGs. In order words, GHGs alone do not drive the applicability of major modification permitting.

However, even if the PTE of NSR-regulated pollutants is estimated to be above the major modification thresholds, a netting analysis can be performed to show that the net emissions increase is not above the SER [65]. A netting analysis would be an appropriate strategy if the petroleum refinery has reduced VOC emissions at some time over the previous five years, and these reductions are enough to offset the emissions increase from modifications to below the SER limit. Any emissions increase over the five-year period would also have to be included in the netting analysis. Such a situation is site-specific and cannot be predicted without using refinery-specific data on past process modifications and operational changes.

3.2.2. Title V permitting

Because all petroleum refineries in the United States are major sources of HAPs and are subject to the NESHAP for petroleum refineries, any petroleum refinery that plans to co-process raw bio-oil would have to revise its current Title V permit to incorporate all compliance requirements; this includes emission standards, monitoring, recordkeeping and reporting requirements in federally applicable air pollution emission standards that apply to the modifications for co-processing raw bio-oil (see Section 3.3 for details). In addition, any requirements contained in an NSR permit, which authorizes the modifications at the petroleum refinery, should also be incorporated in the Title V permit. Once the NSR permit is issued to the petroleum refinery, the modifications to the current Title V permit is a fairly straightforward process.

3.3. Federal air regulation applicability analysis

The modifications required for co-processing raw bio-oil may trigger several U.S. federal air regulatory requirements under NSPS (40 CFR 60) and NESHAP (40 CFR 61 and 63) that could potentially apply to the new equipment and its operation at the petroleum refinery. Table 3 lists

Table 3
U.S. federal emission standards potentially applicable to the new equipment at the petroleum refinery.

Equipment	Target pollutants	Potentially applicable federal emission standards
Storage tanks	VOC, HAP	NSPS (40 CFR 60), Subpart Kb[a] NESHAP (40 CFR 63), Subpart CC[b]
Equipment leaks (e.g., from pumps, valves, and connectors)	VOC, HAP	NSPS (40 CFR 60), Subpart VVa[c] NESHAP (40 CFR 63), Subpart CC[b] NESHAP (40 CFR 61) Subpart J[d]
FCC unit, catalytic reforming units, sulfur recover units, and miscellaneous process vents	VOC, HAP, CO, NO_x, H_2S, PM, PM_{10}, $PM_{2.5}$	NSPS (40 CFR 60), Subpart J[e] and Ja[f] NESHAP (40 CFR 63), Subpart CC[b] NESHAP (40 CFR 63), Subpart UUU[g]

[a] Standards of Performance for Volatile Organic Liquid Storage Vessels (including Petroleum Liquid Storage Vessels) for Which Construction, Reconstruction, or Modification Commenced After July 23, 1984 (40 CFR 60, Subpart Kb) [66].

[b] National Emission Standards for Hazardous Air Pollutants: Petroleum Refineries (40 CFR 63, Subpart CC) [67].

[c] Standards of Performance for Equipment Leaks of VOC in the Synthetic Organic Chemicals Manufacturing Industry for Which Construction, Reconstruction, or Modification Commenced After November 7, 2006 (40 CFR 60, Subpart VVa) [68].

[d] National Emission Standard for Equipment Leaks (Fugitive Emission Sources) of Benzene (40 CFR 61, Subpart J) [69].

[e] Standards of Performance for Petroleum Refineries (40 CFR 60, Subpart J) [70].

[f] National Emission Standards of Performance for Petroleum Refineries for which Construction, Reconstruction, or Modification Commenced after May 14, 2007 (40 CFR 60, Subpart Ja) [71].

[g] National Emission Standards for Hazardous Air Pollutants: Petroleum Refineries (40 CFR 63, Subpart UUU) [72].

all the U.S. federal regulations that could apply to the new equipment, and we discuss their applicability in the following subsections. Because the sites of existing petroleum refineries are geographically diverse, we do not examine the applicability of any state or local air regulations. However, refineries that plan to implement modifications for co-processing bio-oil need to review the applicability criteria of any potentially relevant state or local air regulations.

3.3.1. Federal rules potentially applicable to storage tanks

NSPS Subpart Kb applies to storage vessels with a capacity > 10,566 gallons (40 m^3) that contain volatile organic liquids (including petroleum liquids). However, to be subject to the control requirements in this rule, a tank must have a capacity ≥ 19,813 gallons (75 m^3) and store organic liquids with a maximum true vapor pressure of 27.6 kPa or greater; or a capacity ≥ 39,890 gallons (151 m^3) and storing a liquid with a maximum true vapor pressure of 5.2 kPa or greater. Although the raw bio-oil storage tank at a petroleum refinery is expected to be greater than the capacity threshold (151 m^3), the maximum true vapor pressure of raw bio-oil is expected to be lower than the threshold value of 5.2 kPa. Therefore, the control requirements in 40 CFR 60, Subpart Kb would not apply to the bio-oil storage tank. For tanks that are subject to Subpart Kb but are not subject to the control requirements under this rule, a record of measured values of parameters (e.g., tank dimensions, tank capacity, and any changes in vapor pressure) might need to be maintained.

The NESHAP for petroleum refineries (40 CFR 63, Subpart CC) specifies control requirements for liquid storage vessels that meet certain thresholds for tank size, liquid vapor pressure, and HAP concentration. The storage tank provisions do not apply to the storage of liquids with an annual average HAP concentration ≤ 2% by weight of total organic HAP or with a maximum true vapor pressure less than 3.4 kPa. The organic HAP content of raw bio-oil varies depending on the feedstock used and process used to produce bio-oil. Research by the U.S. Department of Agriculture has shown that the organic HAP concentration of fast pyrolysis bio-oil from wood, switchgrass and late stage-harvested alfalfa is lower than 2% organic HAP [73]. In addition, the maximum true vapor pressure of raw bio-oil is estimated to be lower than the vapor pressure threshold under the rule. Accordingly, the control requirements of Subpart CC are not likely to apply to raw bio-oil storage tanks.

3.3.2. Federal rules potentially applicable to equipment leaks

NSPS Subpart VVa specifies a leak detection and repair program that applies generally to the SOCMI. As the petroleum refineries do not meet the definition of SOCMI, they are not subject to this rule. No other NSPSs covers equipment leaks by petroleum refineries.

NESHAP Subpart CC covers equipment leaks from pumps, compressors, valves, and pressure release devices if the liquid in operation has ≥ 5% by weight concentration of total organic HAP. As discussed in the applicability of NSPS Subpart Kb to storage tanks, raw bio-oil is unlikely to have a HAP concentration equal to or greater than 5% by weight, so Subpart CC would not likely apply to equipment leaks.

NESHAP (40 CFR 61) Subpart J covers equipment leaks from equipment in "benzene service", which is defined as equipment that contains or contacts fluid that is at least 10% benzene. Raw bio-oil is not expected to have a concentration of 10% benzene or more. Therefore, the new equipment is not likely to be subject to Subpart J.

3.3.3. Federal rules potentially applicable to refining processes

The NSPS for petroleum refineries (40 CFR 60, Subparts J and Ja) controls PM, CO, and SO_2 emissions from FCC catalyst regenerators, SO_2 from fuel gas combustion, and SO_2 and reduced sulfur compounds from Claus sulfur recovery plants. Subpart Ja also controls NO_x emissions from fuel gas combustion. Because these NSPS apply to specific refining equipment, the modifications required to co-process bio-oil would not make any of the equipment subject to either NSPS.

The NESHAPs for petroleum refineries (40 CFR 63, Subparts CC and UUU) controls organic HAPs from process vents (e.g., FCC units, catalytic reforming units, sulfur recovery units and miscellaneous equipment specified in the rule), storage vessels, wastewater treatment operations, and equipment leaks (for equipment containing ≥ 5% organic HAP), and inorganic HAP emissions from FCC and catalytic reforming units. Adding a new bio-oil storage tank and feed injector for bio-oil co-processing would not make any other process units subject to either NESHAPs, because as major sources of HAP, all petroleum refineries in the United States are already subject to these NESHAPs.

3.4. Estimating co-processing potential for individual refineries

As elaborated in Section 3.2, for a large number of petroleum refineries, co-processing 5% bio-oil in their FCC unit(s) is not expected to trigger the major modification permitting requirements given that the estimated increases in VOC, PM, PM_{10}, $PM_{2.5}$, and CO emissions are below their respective major modification thresholds. We attempt to understand the raw bio-oil co-processing potential at petroleum refineries in the United States under two criteria: (1) restricting co-processing to a certain level so that the increase in NSR-regulated pollutants would not trigger a major modification permitting requirement and (2) constraining the raw bio-oil co-processing rate to 20% as a technical limit. Fig. 3 shows a map of all the petroleum refineries with FCC units in the United States and their potential to co-process raw bio-oil without triggering major modification permitting requirements. The map also shows the refineries that are located in an extreme ozone NAA and thus cannot co-process any bio-oil in their FCC units without triggering the major modification permitting requirement.

The preliminary results from our analysis indicate that 55 of 95 refineries with FCC units in the United States potentially could co-process raw bio-oil up to 20% without requiring PSD or NNSR permitting. Nine refineries could co-process up to only 5% of raw bio-oil; the lower co-processing potential is due to several factors, including the attainment status of the area where the petroleum refinery is located, higher average ambient temperatures, and larger bio-oil storage tanks being required to be installed. Nevertheless, the results could underestimate raw bio-oil co-processing potential because we use conservatively high assumptions to estimate PTE. For example, we assume a vertical fixed-roof tank for the storage tank and 14-day storage capacity. If petroleum refineries decide to install internal or external floating roof tanks, the emissions could be reduced by more than 90% [74,75], allowing for a higher bio-oil co-processing rate.

By using the two criteria for limiting the co-processing potential of the petroleum refineries, we find that the refineries equipped with FCC units in the United States could co-process 573,000 bbl of raw bio-oil per day (0.79 m^3/sec). As a first order approximation, co-processing this amount of raw bio-oil could have the potential to produce a total of 1.92 billion gallons gasoline equivalent (GGE) of renewable hydrocarbon fuels per year; this figure is estimated based on the yields of gasoline and light-cycle oil at various co-processing rates as well as on the renewable carbon contents in these products via carbon dating (^{14}C) analysis by Pinho et al. [16,17] The 1.92 billion GGE is equivalent to 1.4% of motor gasoline consumption or 18% of total ethanol production in the United States in 2018.

If the petroleum refineries achieve this raw bio-oil co-processing potential, several pollutants including PM (various fractions) and VOC emissions would be expected to increase. To put the magnitudes of the potential emission increase into perspective, we compare them with the current emission levels using data from the EPA's National Emissions Inventory (NEI) database [76]. Our comparison suggests the estimated increases in VOC, PM_{10} and $PM_{2.5}$ emissions are minimal portions (3%, 2.1% and 0.2% respectively) of the total VOC, $PM_{2.5}$ and PM_{10} emissions from petroleum refineries in the United States and therefore that co-processing raw bio-oil is not expected to cause air quality to deteriorate significantly.

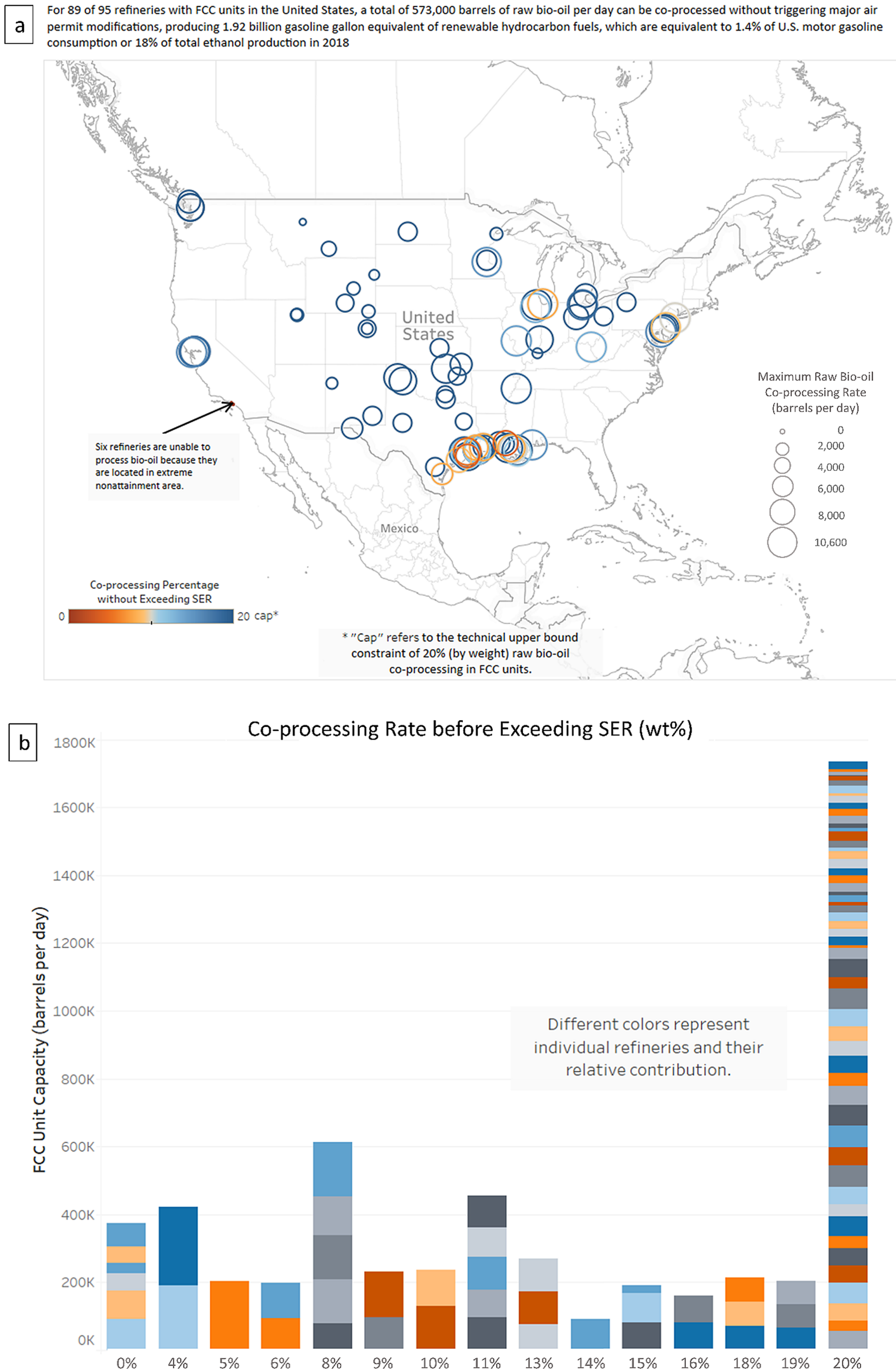

Fig. 3. Petroleum refineries with available co-processing potential without triggering a major modification permitting requirement and upper-bound constraint of 20% raw bio-oil co-processing. Fig. 3a shows the locations of refineries and their co-processing potential. Fig. 3b shows the raw bio-oil co-processing potential (x-axis) relative to fluid catalytic cracking unit capacities (y-axis) for each refinery. The blocks with different colors represent the number of refineries (95 in our case) that can co-process 0 to 20% of raw bio-oil as shown by the values in the x-axis. The height of each block represents the FCC capacity for the refinery. For example, six blocks at point 0 on the x-axis shows six refineries with 373 k bbl/day of FCC capacity that cannot co-process any raw bio-oil as they are located in an extreme ozone nonattainment area.

3.5. Limitations

Although we use the best available information and engineering judgment for our analysis, we stress that there are significant uncertainties inherent in our quantitative estimates that are due to (1) a lack of publicly available information, such as the physicochemical properties (vapor pressure, in particular) of raw bio-oil and (2) the need to estimate the many parameters that are an important part of emissions (e.g., the capacity of the bio-oil storage tank and equipment component counts). In general, we use conservative assumptions to avoid underestimating PTE for air permitting purposes, however, for any petroleum refineries that might apply for an air permit for modifications to co-process bio-oil, site-specific operational data should be used to estimate the changes in emissions. In addition, our regulatory analysis focused exclusively on U.S. federal air regulations that are likely applicable to the modifications to co-process raw bio-oil. Refineries would need to consider requirements and limitations pertaining to state regulations that apply to their facility, equipment units and operations.

In estimating the bio-oil co-processing potential in the United States, we did not consider any technical barriers and risks or operational challenges that could restrict the capability of petroleum refineries to implement bio-oil co-processing. For example, past experiments indicate that the immiscibility of raw bio-oil with VGO because of bio-oil's higher oxygen and water content may prevent refineries from co-processing bio-oil at the level we assumed (i.e., up to 20%) [77]. This technical barrier has been addressed to some extent by using deoxygenation techniques like decarboxylation, decarbonylation, and hydrodeoxygenation to reduce oxygen content in bio-oil as well as by using two separate nozzles for feeding bio-oil and VGO [78–80]. Other barriers include the high acidity of bio-oil, which could lead to the corrosiveness to the FCC unit, and the potential increase in char and coke yields [81–84] (though research has shown this to be reduced by using a different feed nozzle for bio-oil) [29]. Also, the characteristics of renewable fuels produced significantly vary based on fossil feed (VGO) and the origin of bio-based intermediates used for co-processing (bio-oils from fast pyrolysis) [85,86]. As research on co-processing raw bio-oil advances and more information becomes available, key technical parameters could be further defined and incorporated into our analysis to determine the potential of bio-oil co-processing for specific petroleum refineries.

Moreover, the renewable fuel must meet the requirements for American Society for Testing and Materials (ASTM) specifications for use in existing engines [78], even if the regulatory approvals for use of bio-based feed in the refineries and sale of renewable gasoline and diesel products have been approved [87,88]. Last but not least, it should be noted that because co-processing raw bio-oil with VGOs in FCC does not yield two distinguishable streams (i.e., bio-based or fossil products), there is inherent uncertainty in quantifying the renewable content of the products. Emerging methods are under development, including carbon dating, detailed total mass balances for FCC and downstream conversions by each refinery [8,89].

4. Conclusions

Increasing renewable energy content in infrastructure-compatible transportation fuels supports United States biofuel objectives (e.g., renewable fuel standards), provides an option to use domestic biomass feedstocks, as well as offers an important greenhouse gas mitigation pathway. Prior analyses have only considered the potential of co-processing raw bio-oil under the technical limits. In this paper we enhance these prior analyses through detailed consideration of requirements for the existing refineries in terms of air pollutant emissions regulations and permits. Because refineries in the United States may need air permits prior to modifications, there could be reluctance among existing facilities to modify their processes for co-processing raw bio-oil with petroleum-derived vacuum gas oil in fluid catalytic cracking units in a way that triggers major permit modifications because of the cost, time, and uncertainty that new source review permitting may introduce. Thus, our analysis is an important refinement of understanding the potential for co-processing raw bio-oil in existing petroleum refineries that, while specific to U.S. federal regulations, provides a template for how to complete similar analyses if there are additional requirements at the state or local level, or in other countries and jurisdictions based on their specific regulations.

Our analysis provides an initial estimate of raw bio-oil co-processing potential within existing petroleum refineries with fluid catalytic cracking units in the United States. The results show that existing refineries co-processing $\leq$8400 bbl/day (0.012 m^3/sec) of raw bio-oil at a 5% co-processing rate in their fluid catalytic cracking units are not expected to be subject to major modification permitting requirements under the United States Environmental Protection Agency's New Source Review program based on the assumptions stated in the Section 2.2 (e.g., assuming the average ambient temperature of Houston, Texas to estimate volatile organic compound [VOC] emissions from the storage tanks). Also, the modifications would most likely not subject a refinery to any additional New Source Performance Standards or National Emission Standards for Hazardous Air Pollutants to which it is not already complying. This finding is important because it suggests the permitting process is not expected to require changes to existing emission controls at petroleum refineries to comply with current U.S. federal regulations.

These results are extended to determine the upper bound raw bio-oil co-processing potential of each existing petroleum refinery equipped with fluid catalytic cracking units in the United States by imposing two criteria: (1) restricting co-processing to a level such that the emission increase from no pollutant would trigger the requirement for a major modification permit under Prevention of Significant Deterioration or Nonattainment New Source Review programs, and (2) constraining the raw bio-oil co-processing rate to 20% as our upper bound. Our preliminary results indicate that 55 refineries of the 95 refineries with fluid catalytic cracking units in the United States could co-process 20% raw bio-oil without needing to obtain a major modification permit. The other 34 refineries could co-process 4–20% raw bio-oil, while the 6 refineries in the extreme ozone nonattainment areas could not implement co-processing without triggering a major modification permitting requirement.

Within limits (i.e., the technical and permitting criteria considered), we find that petroleum refineries in the United States have the potential to co-process 573,000 bbl/day (0.79 m^3/sec) of raw bio-oil in their fluid catalytic cracking units to produce partially renewable and infrastructure compatible transportation fuels. Based on our first-order approximation calculations [17,90,91], this represents 1.92 billion gallons gasoline equivalent per year (0.23 m^3/sec) of renewable hydrocarbon fuels, which is equivalent to 1.4% of United States gasoline consumption or 18% of total ethanol production in 2018. This implies a maximum potential bio-oil co-processing rate of 13% (fluid catalytic cracking capacity-weighted average) in the United States. If we assume this co-processing rate is applicable to all refineries on a global scale, 3 billion gallons gasoline equivalent per year (0.36 m^3/sec) of renewable hydrocarbon fuel could be produced from existing infrastructure annually, which represents 11% of global ethanol production in 2018.

Our analysis sheds lights into how process modifications to co-process bio-oil at existing refineries could affect air emissions while addressing permitting concerns for petroleum refineries wanting to leverage their facilities to produce partially renewable hydrocarbon fuels. Considering all refineries equipped with fluid catalytic cracking units in the United States, our results provide an upper bound estimate of co-processing potential with minimum regulatory requirements for the petroleum refineries. Our findings could help refineries integrate renewable fuels in their operations utilizing existing infrastructure while limiting risks and help stakeholders make informed decisions and develop strategies to expedite the permitting process. This knowledge would save time and mitigate the risks associated with possible delays in obtaining the necessary permits to start the retrofit for raw bio-oil co-processing. However, we stress that our work addresses only one important aspect, which would affect refineries' investment decision regarding bio-oil co-processing. Technical feasibilities and economics of bio-oil co-processing are important factors to consider in any decision-marking by a refinery but are beyond the scope of this study.

CRediT authorship contribution statement

Arpit H. Bhatt: Conceptualization, Writing - original draft, Writing - review & editing. **Yimin Zhang:** Conceptualization, Writing - original draft, Writing - review & editing. **Garvin Heath:** Conceptualization, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apenergy.2020.114937.

References

[1] European Commission. Renewable Energy – Recast to 2030 (RED II). https://ec.europa.eu/jrc/en/jec/renewable-energy-recast-2030-red-ii; 2016.

[2] Office of Journal of European Union. Directive (EU) 2018/2001 of the European Parliament and of the Council of 11 December 2018 on the promotion of the use of energy from renewable sources. https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=uriserv:OJ.L_.2018.328.01.0082.01.ENG&toc=OJ:L:2018:328:TOC; 2018.

[3] EPA. Renewable Fuel Standard Program. https://www.epa.gov/renewable-fuel-standard-program; 2017.

[4] U.S. Department of Energy. 2016 Billion-Ton Report: Advancing Domestic Resources for a Thriving Bioeconomy, Volume 1: Economic Availability of Feedstocks. Oak Ridge, TN: Oak Ridge National Laboratory (ORNL); 2016.

[5] Maity SK. Opportunities, recent trends and challenges of integrated biorefinery: Part I. Renew Sustain Energy Rev 2015;43:1427–45. https://doi.org/10.1016/j.rser.2014.11.092.

[6] Stefanidis SD, Kalogiannis KG, Lappas AA. Co-processing bio-oil in the refinery for drop-in biofuels via fluid catalytic cracking. Wiley Interdisciplinary Rev: Energy Environ 2017;7:e281. https://doi.org/10.1002/wene.281.

[7] Beims R, Bertoli S, Botton V, Ender L, Simionatto E, Meier HF, et al. Co-processing of thermal cracking bio-oil at petroleum refineries 2017;11. 10.5419/bjpg2017-0009.

[8] CARB (California Air Resource Board). Co-processing of Biogenic Feedstocks in Petroleum Refineries; 2017. https://www.arb.ca.gov/fuels/lcfs/lcfs_meetings/020717_staffdiscussionpaper.pdf.

[9] Corma A, Martínez C, Melo FV, Sauvanaud L, Carriat JY. A new continuous laboratory reactor for the study of catalytic cracking. Appl Catal A 2002;232(1-2):247–63. https://doi.org/10.1016/S0926-860X(02)00110-2.

[10] Corma A, Sauvanaud L. FCC testing at bench scale: new units, new processes, new feeds. Catalysis Today 2013;218–219:107–14. https://doi.org/10.1016/j.cattod.2013.03.038.

[11] Nee JRD, Harding RH, Yaluris G, Cheng W-C, Zhao X, Dougan TJ, et al. Fluid Catalytic Cracking (FCC). Catal Addit 2004. https://doi.org/10.1002/0471238961.fluidnee.a01.

[12] Bertero M, Sedran U. Chapter 13 - Coprocessing of bio-oil in fluid catalytic cracking A2: pandey, ashok. In: Bhaskar T, Stöcker M, Sukumaran RK, editors. Recent Advances in Thermo-Chemical Conversion of Biomass, Boston: Elsevier; 2015, p. 355–81. 10.1016/B978-0-444-63289-0.00013-2.

[13] Lindfors C, Paasikallio V, Kuoppala E, Reinikainen M, Oasmaa A, Solantausta Y. Co-processing of dry bio-oil, catalytic pyrolysis oil, and hydrotreated bio-oil in a micro activity test unit. Energy Fuels 2015;29:3707–14. https://doi.org/10.1021/acs.energyfuels.5b00339.

[14] Almeida M, Pinho A. Co-processing of Fast Pyrolysis Oil in FCC for Transportation Fuels, Empyro Symposium. https://www.researchgate.net/publication/277715466_Co-processing_of_fast_pyrolysis_oil_in_FCC_for_transportation_fuels; 2015.

[15] Bryden K, Weatherbee G, Habib ET. Flexible Pilot Plant Technology for Evaluation of Unconventional Feedstocks and Processes. vol. 113; 2013.

[16] Pinho A de R, de Almeida MBB, Mendes FL, Ximenes VL, Casavechia LC. Co-processing Raw Bio-oil and Gasoil in an FCC Unit. Fuel Processing Technology 2015;131:159–66. 10.1016/j.fuproc.2014.11.008.

[17] de Pinho A, de Almeida MBB R, Mendes FL, Casavechia LC, Talmadge MS, Kinchin CM. Fast pyrolysis oil from pinewood chips co-processing with vacuum gas oil in an FCC unit for second generation fuel production. Fuel 2017;188:462–73. https://doi.org/10.1016/j.fuel.2016.10.032.

[18] Ibarra Á, Hita I, Azkoiti MJ, Arandes JM, Bilbao J. Catalytic cracking of raw bio-oil under FCC unit conditions over different zeolite-based catalysts. J Ind Eng Chem 2019;78:372–82. https://doi.org/10.1016/j.jiec.2019.05.032.

[19] Ibarra Á, Hita I, Arandes JM, Bilbao J. Influence of the composition of raw bio-oils on their valorization in fluid catalytic cracking conditions. Energy Fuels 2019;33:7458–65. https://doi.org/10.1021/acs.energyfuels.9b01527.

[20] Frey S. Production of transportation fuels by co-processing biomass-derived pyrolysis oils in a petroleum refinery fluid catalytic cracking unit. TC Biomass 2015.

[21] Wissinger R. Production of Renewable Fuels from Biomass by FCC Co-Processing; 2014. https://www.energy.gov/sites/prod/files/2014/11/f19/wissinger_biomass_2014.pdf.

[22] Market Prospects, Oil & Gas. Technip to Design and Build Pyrolysis Plants for BTG Bioliquids. Pump Industry Analyst 2016;2016:2. 10.1016/S1359-6128(16)30216-6.

[23] EPA. Release of Interim Policy on Federal Enforceability of Limitations on Potential to Emit; 1996. https://www.epa.gov/sites/production/files/2015-08/documents/pottoemi.pdf.

[24] EPA. New Source Review (NSR) Permitting. http://www.epa.gov/nsr.

[25] EPA. Overview of the Clean Air Act and Air Pollution. https://www.epa.gov/clean-air-act-overview; 2015.

[26] EPA. The Clean Air Act in a Nutshell: How It Works. http://www.epa.gov/air/caa/pdfs/CAA_Nutshell.pdf; 2013.

[27] National EPA. Emission standards for hazardous air pollutants from petroleum refineries; proposed rule. Federal Register Notice 2007.

[28] Ibarra Á, Rodríguez E, Sedran U, Arandes JM, Bilbao J. Synergy in the cracking of a blend of bio-oil and vacuum gasoil under fluid catalytic cracking conditions. Ind Eng Chem Res 2016;55:1872–80. https://doi.org/10.1021/acs.iecr.5b04502.

[29] Pinho A de R, de Almeida Marlon Brando Bezerra, Mendes Fabio Leal, Ximenes Vitor Loureiro. Production of lignocellulosic gasoline using fast pyrolysis of biomass and a conventional refining scheme. Pure Appl Chem 2014;86:859–65. 10.1515/pac-2013-0914.

[30] Freeman CJ, Jones SB, Padmaperuma AB, Santosa DM, Valkenburg C, Shinn J. Initial Assessment of U.S. Refineries for Purposes of Potential Bio-Based Oil Insertions. Pacific Northwest National Lab. (PNNL), Richland, WA (United States); 2013. 10.2172/1097335.

[31] EIA (Energy Information Administration). Refinery Capacity Report. https://www.eia.gov/petroleum/refinerycapacity/table3.pdf; 2018.

[32] Lian X, Xue Y, Zhao Z, Xu G, Han S, Yu H. Progress on upgrading methods of bio-oil: a review: upgrading progress of bio-oil. Int J Energy Res 2017;41:1798–816.

https://doi.org/10.1002/er.3726.
[33] Steele P, Puettmann ME, Penmetsa VK, Cooper JE. Life-cycle assessment of pyrolysis bio-oil production. Forest Product J 2012;62(326–34). https://doi.org/10.13073/FPJ-D-12-00016.1.
[34] Lehto J, Oasmaa A, Solantausta Y, Kytö M, Chiaramonti D. Review of fuel oil quality and combustion of fast pyrolysis bio-oils from lignocellulosic biomass. Appl Energy 2014;116:178–90. https://doi.org/10.1016/j.apenergy.2013.11.040.
[35] Jones SB, Meyer PA, Snowden-Swan LJ, Padmaperuma AB, Tan E, Dutta A, et al. Process Design and Economics for the Conversion of Lignocellulosic Biomass to Hydrocarbon Fuels: Fast Pyrolysis and Hydrotreating Bio-Oil Pathway. Pacific Northwest National Laboratory (PNNL), Richland, WA (US); 2013.
[36] Gollakota ARK, Kishore N, Gu S. A review on hydrothermal liquefaction of biomass. Renew Sustain Energy Rev 2018;81:1378–92. https://doi.org/10.1016/j.rser.2017.05.178.
[37] Ensyn. Refinery Feedstocks - Low Carbon Transportation Fuels. http://www.ensyn.com/refinery-feedstocks.html.
[38] UOP, LLC. Final Project Report - Pilot-Scale Biorefinery: Sustainable Transport Fuels from Biomass and Algal Residues via Integrated Pyrolysis, Catalytic Hydroconversion and Co-processing with Vacuum Gas Oil; 2016. https://www.osti.gov/servlets/purl/1267107.
[39] Chum HL, Pinho A. DOE Bioenergy Technologies Office (BETO) 2015 Project Peer Review. 2.4.2.303 Brazil Bilateral: Petrobras-NREL CRADA; 2015. https://www.energy.gov/sites/prod/files/2015/04/f21/thermochemical_conversion_chum_242303.pdf.
[40] EPA. Emissions Factors & AP 42, Compilation of Air Pollutant Emission Factors; 1995. https://www.epa.gov/air-emissions-factors-and-quantification/ap-42-compilation-air-emissions-factors.
[41] Fogassy G, Thegarid N, Schuurman Y, Mirodatos C. From biomass to bio-gasoline by FCC co-processing: effect of feed composition and catalyst structure on product quality. Energy Environ Sci 2011;4:5068–76. https://doi.org/10.1039/C1EE02012A.
[42] EPA. AP42, Section 13.2.2 Unpaved Roads - Updated November 2006; 2006. http://www.epa.gov/ttn/chief/ap42/ch13/final/c13s0202.pdf.
[43] EPA. TANKS Emissions Estimation Software, Version 4.09D; 2006. http://www.epa.gov/ttnchie1/software/tanks/.
[44] CIRAD. Material Safety Data Sheet for Bio-oil; 2006. http://www.pyne.co.uk/Resources/user/docs/CIRAD_MSDS-Final.pdf.
[45] Oasmaa A, Peacocke C. Properties and fuel use of biomass-derived fast pyrolysis liquids – a guide. VTT Journal 2010.
[46] Nolan D. Handbook of Fire and Explosion Protection Engineering Principles. Second; 2010.
[47] Goteti AC. Experimental Investigation and Systems Modeling of Fractional Catalytic Pyrolysis of Pine [Thesis]. Georgia Institute of Technology; 2010 https://smartech.gatech.edu/handle/1853/42844.
[48] Brown OLI. The Clausius-Clapeyron equation. J Chem Educ 1951;28:428. https://doi.org/10.1021/ed028p428.
[49] Thangalazhy-Gopakumar S, Adhikari S, Ravindran H, Gupta RB, Fasina O, Tu M, et al. Physiochemical properties of bio-oil produced at various temperatures from pine wood using an auger reactor. Bioresour Technol 2010;101:8389–95. https://doi.org/10.1016/j.biortech.2010.05.040.
[50] EPA. Potential to Emit – A Guide for Small Businesses; 1998. https://www3.epa.gov/airtoxics/1998sbapptebroc.pdf.
[51] EPA. Protocol for Equipment Leak Emission Estimates; 1995. http://www.epa.gov/ttnchie1/efdocs/equiplks.pdf.
[52] EPA. Control Techniques for Carbon Monoxide Emissions; 1979. https://nepis.epa.gov/Exe/ZyNET.exe/00001Z4I.TXT?ZyActionD=ZyDocument&Client=EPA&Index=1976+Thru+1980&Docs=&Query=&Time=&EndTime=&SearchMethod=1&TocRestrict=n&Toc=&TocEntry=&QField=&QFieldYear=&QFieldMonth=&QFieldDay=&IntQFieldOp=0&ExtQFieldOp=0&XmlQuery=&File=D%3A%5Czyfiles%5CIndex%20Data%5C76thru80%5CTxt%5C00000001%5C00001Z4I.txt&User=ANONYMOUS&Password=anonymous&SortMethod=h%7C-&MaximumDocuments=1&FuzzyDegree=0&ImageQuality=r75g8/r75g8/x150y150g16/i425&Display=hpfr&DefSeekPage=x&SearchBack=ZyActionL&Back=ZyActionS&BackDesc=Results%20page&MaximumPages=1&ZyEntry=1&SeekPage=x&ZyPURL.
[53] EPA. RACT/BACT/LAER Clearinghouse (RBLC). http://cfpub.epa.gov/rblc/.
[54] Stefanidis SD, Kalogiannis KG, Lappas AA. Co-processing Bio-oil in the Refinery for Drop-in Biofuels via Fluid Catalytic Cracking. WIREs Energy Environ 2018:7:281. 10.1002/wene.281.
[55] Minnesota Pollution Control Agency. Facts about Determining Applicability of New Source Review; 2010. https://www.pca.state.mn.us/sites/default/files/aq4-25.pdf.
[56] EPA. Fact Sheet: New Source Review (NSR). https://www.epa.gov/sites/production/files/2015-12/documents/nsrbasicsfactsheet103106.pdf.
[57] EPA. The Green Book Nonattainment Areas for Criteria Pollutants. http://www3.epa.gov/airquality/greenbook/index.html.
[58] EPA. Findings of Failure to Submit State Implementation Plan Submittals for the 2008 Ozone National Ambient Air Quality Standards (NAAQS). Federal Register; 2017. https://www.federalregister.gov/documents/2017/02/03/2017-02188/findings-of-failure-to-submit-state-implementation-plan-submittals-for-the-2008-ozone-national.
[59] URS Corporation J. Environmental Impact Report for the ExxonMobil Torrance Refinery Rule 1105.1 Compliance Project: South Coast Air Quality Management District 2007:75.
[60] EPA. AP42 7.1 Organic Liquid Storage Tanks. Nov 2006 update. Correction 8/12 eq. 2-20.pdf. http://www.epa.gov/ttn/chief/ap42/ch07/final/c07s01.pdf; 2006.
[61] EPA. Air Pollution Control Technology Fact Sheet, EPA-452/F-03-022; 2003. http://www.epa.gov/ttn/catc/dir1/fthermal.pdf.
[62] EPA. Air Pollution Control Technology Fact Sheet, EPA-452/F-03-018; 2003. http://www.epa.gov/ttn/catc/dir1/fcataly.pdf.
[63] EPA. Air Pollution Control Technology Fact Sheet, EPA-452/F-03-016; 2003. http://www.epa.gov/ttn/catc/dir1/fsprytwr.pdf.
[64] EPA. Air pollution Control Technology Fact Sheet, EPA-452/F-03-019; 2003. http://www.epa.gov/ttn/catc/dir1/fflare.pdf.
[65] Pruit, E. Scott. Project Emissions Accounting Under the New Source Review Preconstruction Permitting Program; 2018. https://www.epa.gov/nsr/project-emissions-accounting-under-new-source-review-preconstruction-permitting-program.
[66] Code of Federal Regulations. 40 CFR 60 Subpart Kb - Standards of Performance for Volatile Organic Liquid Storage Vessels (Including Petroleum Liquid Storage Vessels) for which Construction, Reconstruction, or Modification Commenced after July 23, 1984; 1987. http://www.ecfr.gov/cgi-bin/text-idx?SID=0eb08c9b43711fe764d454115c6169a9&mc=true&node=sp40.7.60.k_0b&rgn=div6.
[67] Code of Federal Regulations. 40 CFR 63 Subpart CC - National Emission Standards for Hazardous Air Pollutants from Petroleum Refineries; 1995. https://www.ecfr.gov/cgi-bin/text-idx?c=ecfr;rgn=div6;view=text;node=40%3A11.0.1.1.1.3;idno=40;sid=d32b1cc8671aec0365154113b9b47d1a;cc=ecfr.
[68] Code of Federal Regulations. 40 CFR 63 Subpart VVa - Standards of Performance for Equipment Leaks of VOC in the Synthetic Organic Chemicals Manufacturing Industry for Which Construction, Reconstruction, or Modification Commenced After November 7, 2006; 2007. https://www.ecfr.gov/cgi-bin/text-idx?node=sp40.7.60.vv_0a.
[69] Code of Federal Regulations. 40 CFR 61 Subpart J - National Emission Standard for Equipment Leaks (Fugitive Emission Sources) of Benzene; 1984. https://ECFR.io/Title-40/pt40.10.61.
[70] Code of Federal Regulations. 40 CFR 60 Subpart J - Standards of Performance for Petroleum Refineries; 2012. https://www.ecfr.gov/cgi-bin/text-idx?node=sp40.7.60.j.
[71] Code of Federal Regulations. 40 CFR 60 Subpart Ja - Standards of Performance for Petroleum Refineries for Which Construction, Reconstruction, or Modification Commenced After May 14, 2007; 2008. https://www.ecfr.gov/cgi-bin/text-idx?node=sp40.7.60.j_0a.
[72] Code of Federal Regulations. 40 CFR 63 Subpart UUU - National Emission Standards for Hazardous Air Pollutants for Petroleum Refineries: Catalytic Cracking Units, Catalytic Reforming Units, and Sulfur Recovery Units; 2002. https://www.ecfr.gov/cgi-bin/retrieveECFR?gp=&r=SUBPART&n=40y13.0.1.1.1.5.
[73] Mullen CA, Boateng A. Fast Pyrolysis and Bio-oil Production from Agricultural Residues and Energy Crops; 2008. https://www.ars.usda.gov/ARSUserFiles/50100500/errc-p2.pdf.
[74] EPA. Hazardous Air Pollutant Emissions from Process Units in the Synthetic Organic Chemical Manufacturing Industry- Background Information for Proposed Standards, Volume 1B: Control Technologies, EPA-453/D-92-016B; 1992. http://nepis.epa.gov/Exe/ZyPDF.cgi/2000H2DY.PDF?Dockey=2000H2DY.PDF.
[75] EPA. Alternative Control Techniques Document: Volatile Organic Liquid Storage in Floating and Fixed Roof Tanks, EPA-453/R-94-001; 1994. http://www.epa.gov/glo/SIPToolkit/ctg_act/199401_voc_epa453_r-94-001_liquid_storage_roof_tanks.pdf.
[76] EPA. National Emissions Inventory (NEI) | Air Emissions Inventories. https://www.epa.gov/air-emissions-inventories/national-emissions-inventory-nei; 2018.
[77] Graça I, Lopes JM, Cerqueira HS, Ribeiro MF. Bio-oils upgrading for second generation biofuels. Industrial and Engineering Chemistry Research 2013;52:275–87. 10.1021/ie301714x.
[78] Talmadge MS, Baldwin RM, Biddy MJ, McCormick RL, Beckham GT, Ferguson GA, et al. A perspective on oxygenated species in the refinery integration of pyrolysis oil. Green Chem 2014;16:407–53. https://doi.org/10.1039/C3GC41951G.
[79] Melero JA, Iglesias J, Garcia A. Biomass as renewable feedstock in standard refinery units. Feasibility, opportunities and challenges. Energy Environ Sci 2012;5:7393–420. https://doi.org/10.1039/C2EE21231E.
[80] Huber GW, Corma A. Synergies between bio- and oil refineries for the production of fuels from biomass. Angew Chem Int Ed 2007;46:7184–201. https://doi.org/10.1002/anie.200604504.
[81] Vitolo S, Bresci B, Seggiani M, Gallo MG. Catalytic upgrading of pyrolytic oils over HZSM-5 zeolite: behaviour of the catalyst when used in repeated upgrading-regenerating cycles. Fuel 2001;80:17–26. https://doi.org/10.1016/S0016-2361(00)00063-6.
[82] Gayubo AG, Aguayo AT, Atutxa A, Valle B, Bilbao J. Undesired components in the transformation of biomass pyrolysis oil into hydrocarbons on an HZSM-5 zeolite catalyst. J Chem Technol Biotechnol 2005;80:1244–51. https://doi.org/10.1002/jctb.1316.
[83] Adjaye JD, Katikaneni SPR, Bakhshi NN. Catalytic conversion of a biofuel to hydrocarbons: effect of mixtures of HZSM-5 and silica-alumina catalysts on product distribution. Fuel Process Technol 1996;48:115–43. https://doi.org/10.1016/S0378-3820(96)01031-4.
[84] Adjaye JD, Bakhshi NN. Production of hydrocarbons by catalytic upgrading of a fast pyrolysis bio-oil. Part I: conversion over various catalysts. Fuel Process Technol

1995;45:161–83. https://doi.org/10.1016/0378-3820(95)00034-5.
[85] Van Dyk S, Su J, Mcmillan JD, Saddler (John) J. Potential synergies of drop-in biofuel production with further co-processing at oil refineries. Biofuels, Bioprod Biorefin 2019;13:760–75. https://doi.org/10.1002/bbb.1974.
[86] Manara P, Bezergianni S, Pfisterer U. Study on phase behavior and properties of binary blends of bio-oil/fossil-based refinery intermediates: a step toward bio-oil refinery integration. Energy Convers Manage 2018;165:304–15. https://doi.org/10.1016/j.enconman.2018.01.023.
[87] Biomass Magazine. Ensyn Receives Key Regulatory Approvals from CARB. http://biomassmagazine.com/articles/12874/ensyn-receives-key-regulatory-approvals-from-carb; 2016.
[88] Biofuels Digest. EPA Grants Ensyn Title 40 CFR Approval for RFGasoline. http://www.biofuelsdigest.com/bdigest/2015/11/25/epa-grants-ensyn-title-40-cfr-approval-for-rfgasoline/; 2015.
[89] Schimmel M, Toop G, Alberici S, Koper M. Determining the Renewability of Co-processed Fuels - ECOFYS. https://ec.europa.eu/energy/sites/ener/files/documents/co-processing_final_report_090418.pdf; 2018.
[90] EIA (Energy Information Administration). Petroleum & Other Liquids. https://www.eia.gov/dnav/pet/pet_cons_psup_dc_nus_mbbl_a.htm; 2018.
[91] EIA (Energy Information Administration). Monthly Energy Review. https://www.eia.gov/totalenergy/data/monthly/index.php#renewable; 2018.