Air Pollutant Emissions and Regulatory Implications of a Biorefinery Co-Processing Bio-Oil in a Petroleum Refinery

Preprint

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National Renewable Energy Laboratory

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Air Pollutant Emissions and Regulatory Implications of a Biorefinery Co-Processing Bio-Oil in a Petroleum Refinery

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INTRODUCTION

Pyrolysis oil, also referred to as bio-oil, can be derived from biomass through a fast pyrolysis process and; has attracted considerable attention because of the high carbonaceous matter and high heating value compared to the original biomass.[1–3] Pyrolysis oil provides a viable link between the agriculture/forestry and (petro-) chemical industry. Utilizing the existing fossil fuel infrastructure by introducing raw or partially upgraded bio-oil in the fluidized catalytic cracking unit (FCCU) in petroleum refineries to produce renewable hydrocarbon fuels (i.e., repurposing existing assets) is feasible due to its relatively low capital requirement.[1,4] However, co-processing bio-oil with vacuum gas oil (VGO) in an FCCU may require changes to the process configurations in the petroleum refinery and may emit additional air pollutants that could impact the environment and public health. Based on the type and magnitude of the regulated pollutants emitted, the petroleum refinery may be subject to additional regulations under the New Source Performance Standards (NSPS) or National Emission Standards for Hazardous Air Pollutants (NESHAP) for New Source Review (NSR) and/or Title V program.[5,6] This paper examines the potential regulatory implications (in terms of emissions and federal regulations) that a petroleum refinery would go through when co-processing bio-oil in their FCCU.

In this analysis, we examine the air pollutant emissions for a biorefinery utilizing an ex-situ upgrading of pyrolysis vapors process (hereafter referred as ex situ fast pyrolysis) to produce partially upgraded bio-oil, with a design capacity of 2,000 dry metric tons of biomass per day.[7] Such a biorefinery is capable of providing sufficient bio-oil to a petroleum refinery with an FCCU capacity of up to 4,200 barrels per day if the bio-oil is assumed to be co-processed at a 5% (by volume) feed rate. We evaluate the potential air pollutant regulatory and permitting implications for two potential scenarios: the first case assumes that an ex-situ fast pyrolysis biorefinery is co-located with a petroleum refinery (both facilities are considered to be a single source), and the second case assumes that a petroleum refinery will receive bio-oil from an offsite supplier. We estimate the potential-to-emit (PTE) for 4 FCCU sizes and assess technically feasible emission control options that could be adopted to avoid being subject to Prevention of Significant Deterioration (PSD) requirements due to petroleum refinery modifications to co-process bio-oil. The aim of the research is expected to fill information gaps and overcome barriers related to the air permitting requirements for co-processing bio-oil in existing refineries. The insights gained from this analysis could help expedite permitting processes for petroleum refineries, which seek opportunities to produce low carbon fuels in their existing infrastructure.[1]

METHODS

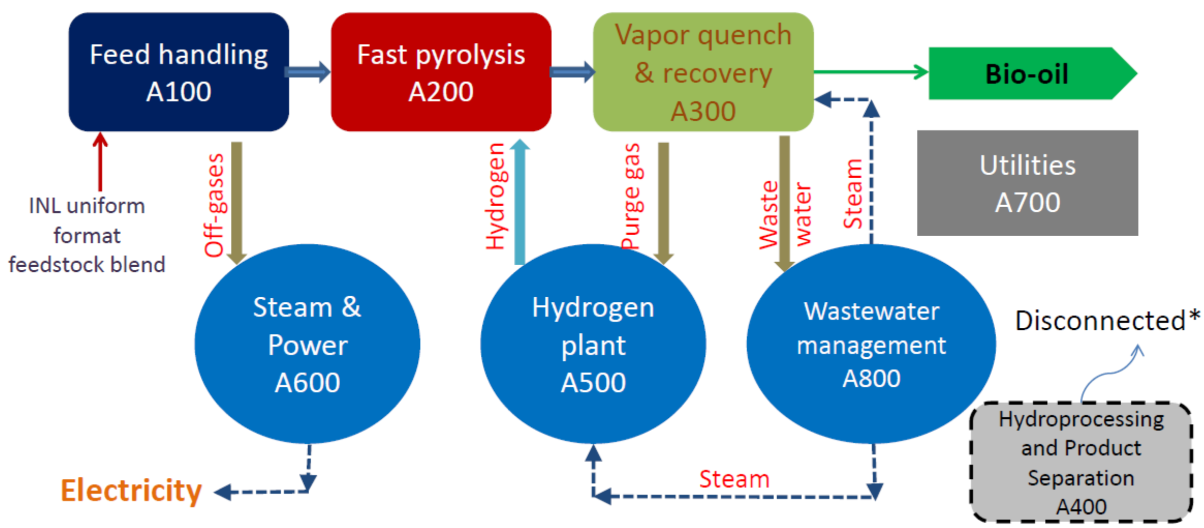
We describe the two scenarios and the methods to estimate the potential-to-emit (PTE) for each scenario in the following sections.

Scenario 1 – Co-locating a bio-oil producing facility with an existing petroleum refinery

Step 1: A baseline process design case to produce partially upgraded bio-oil

The ex-situ fast pyrolysis process to produce partially upgraded bio-oil is divided into 8 process areas: 1) feed handling, 2) fast pyrolysis and vapor upgrading, 3) product recovery, 4) hydroprocessing and product separation, 5) hydrogen plant, 6) steam and power generation, 7) utilities, and 8) wastewater management (refer to Figure 1). Dried and heated biomass is fed to the non-catalytic fast pyrolysis reactor followed by a separate ex-situ catalytic vapor upgrading reactor to produce pyrolysis vapors with low oxygen content. The vapors are quenched in the series of absorbers to separate the organic fraction (partially upgraded bio-oil) from the non-condensable gases. The partially upgraded bio-oil is separated from the aqueous phase and all the off-gases from different areas of the design plant are collected and utilized in the methane reformer to produce hydrogen. It is assumed that the process produces partially upgraded bio-oil as a final product and does not include any hydrotreating and hydrocracking operations.

Figure 1. Overview of the ex-situ fast pyrolysis conversion process producing bio-oil



INL = Idaho National Laboratory

We reviewed the United States Energy Information Administration (U.S. EIA)[8] database on refinery FCCU capacities in the U.S. and divide the biorefinery production capacity into four sizes (refer to Table 1). We estimate the PTE for these four biorefinery sizes by adjusting the emissions by the production capacity ratios using the 4,200 barrels of bio-oil per day production as the base case.

Table 1. Number of petroleum refineries co-processing 5% bio-oil corresponding to four biorefinery production scales

5% of Fluidized Catalytic Cracking Feed Rate (barrels per day)	# of Refineries (% of total refineries with FCC units)
≤1400	32 (34%)
≤2700	51 (54%)
≤4200 (base case)	73 (77%)
≤11625	95 (100%)

Step 2: Estimation of PTE for the ex-situ fast pyrolysis process

We analyze each unit operation in the process to determine the air pollutants likely to be emitted from the process design. We consider the planned emission controls and also identify additional potential control technologies to reduce the emissions below major source threshold (100 tons per year for criteria air pollutants and 25 tons per year for hazardous air pollutants [HAPs]) using EPA's Reasonably Available Control Technology/Best Available Control Technology/Lowest Achievable Emission Rate Clearinghouse database,[12] analogous air permit applications, and other EPA documentation. We estimate the PTE and determine the permitting classification (major or minor) using various sources including Environmental Protection Agency's (EPA's) AP-42 database,[9] material balance from Aspen Plus,[10] and source specific models (such as TANKS 4.09d).[11]

Step 3: Process modifications required for the co-located scenario

For the co-located scenario, we assume that the biorefinery and the petroleum refinery meet the single source determination criteria and would be considered a single source. Some process changes would be required to the baseline bio-oil process design case and petroleum refinery to co-process bio-oil. The biorefinery would not need bio-oil to be loaded into trucks or product truck traffic as the co-located biorefinery would provide bio-oil for co-processing onsite using a pipeline. Also, modifications would be needed to the FCCU to inject the bio-oil into the riser reactor at a different height (new feed injector) than the petroleum feedstock in order to increase thermal cracking and avoid undesirable reactions.

Step 4: Estimate changes in PTE and permitting ramifications for the co-located scenario

EPA has determined that all the petroleum refineries with FCCUs in the U.S. are major sources of HAP under the Title V and NSR permitting program.[13] Therefore, the biorefinery would be subject to the applicability thresholds of Miscellaneous Organic NESHAP (MON), 40 CFR 63, Subpart FFFF.[14] We adjust the emissions by applying the emissions limits required by MON and remove the process areas, that are not needed when the petroleum refinery and the bio-oil facility are co-located. We also adjust the PTE by eliminating emissions associated with the loading operations and product truck traffic as those areas are no longer required in the co-located biorefinery. In addition, the storage tank emissions would change as we assume the biorefinery to be located in Houston, TX, which has a high concentration of petroleum refineries.

We then review the program requirements and permitting criteria under the NSR and Title V program to determine the permitting ramifications for the co-located scenario. We compare the incremental emissions to the Significant Emissions Rate (SER) for attainment areas or Nonattainment NSR (NNSR) major source modification rate for nonattainment areas. In addition, we identify potential controls or combination of control options for pollutants exceeding the major modification threshold for the petroleum refinery to avoid major modification permitting requirements.

Scenario 2 – Co-processing bio-oil in a petroleum refinery shipped from an offsite facility

Step 1: Process modifications required for co-processing bio-oil shipped from an offsite facility

There are several process changes required in the petroleum refinery when the bio-oil is shipped from an offsite facility and co-processed in the refinery. This includes additional storage tanks for bio-oil, associated piping and equipment for transferring bio-oil to the FCCU, a new feed injector for the bio-oil in the FCCU, and increased truck traffic for the bio-oil delivery from an offsite facility.

Step 2: Estimate increase in emissions and permitting ramifications for co-processing bio-oil shipped from an offsite facility

We estimate additional emissions from the process changes described above using various sources including the Environmental Protection Agency's (EPA's) AP-42 database,[9] material balance from Aspen Plus,[10] and source-specific models (such as TANKS 4.09d).[11]

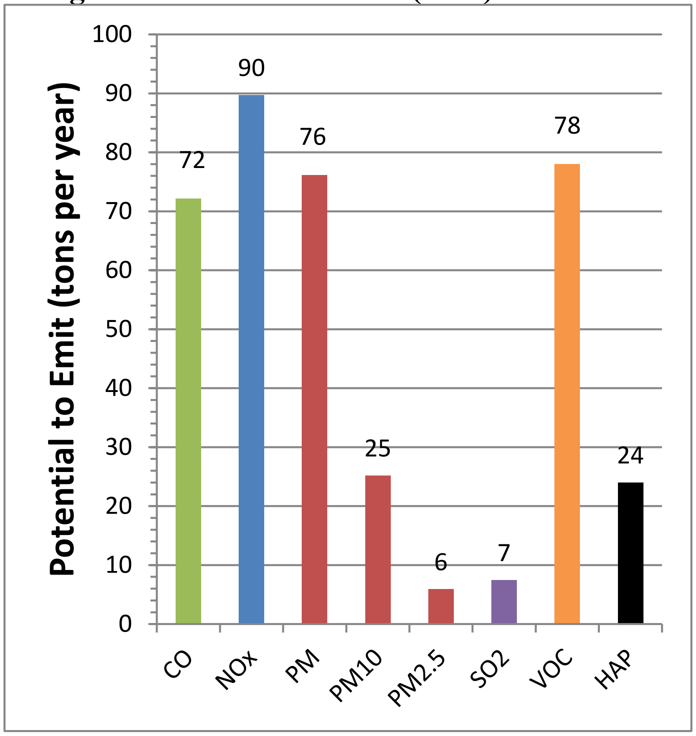
We then follow the same methodology as described in the co-located scenario (Scenario 1) to determine the permitting ramifications under the Title V and NSR program and identify the potential control options to avoid major source modification. We also review the applicability criteria of each potentially applicable federal regulation under NSPS and NESHAP to determine its applicability to the new equipment added due to process changes required for co-processing.

RESULTS

PTE estimates for the ex situ fast pyrolysis design process

Figure 2 shows the PTE estimates for the baseline ex-situ fast pyrolysis design case that produces partially upgraded bio-oil for co-processing in the FCCU of the petroleum refinery. The planned and additional emissions controls considered in the PTE estimation are also summarized in Figure 2.

Figure 2. Potential-to-emit (PTE) estimates for the ex situ fast pyrolysis process design



Equipment	Emission Controls
Planned	
Combustor, Regenerator	Baghouse (PM)
Dryer	Flue gas scrubber (SO_2)
Ash & Sand handling	Ash cooler (PM)
Wastewater treatment	RTO (VOC/HAP)
Additional Controls	
Dryer	Baghouse (PM) Absorber (VOC/HAP)
Combustor, Regenerator	Baghouse (PM)
Wastewater treatment	RTO (VOC/HAP)
Methane reformer	SNCR (NO_x)
Loading Operations	VRU (VOC/HAP)

RTO = regenerative thermal oxidizer, SNCR = selective non-catalytic reduction, VRU = vapor recovery unit

Changes in PTE and permitting ramifications for the co-located scenario

As all the petroleum refineries with FCCUs are major sources of HAP, MON (40 CFR 63, Subpart FFFF) would apply to the biorefinery as well since both the facilities are considered to be single source. Under MON, the biorefinery would need to reduce emissions from continuous operations (dryer vent) by 98%. The biorefinery would also need to reduce HAP emissions from cooling tower and equipment leaks by following the work practice standards required by MON. In addition, PM emissions from cooling towers would also need to be reduced, which could be achieved using high-efficiency drift eliminators. Table 2 summarizes the estimated changes in PTE for the co-located scenario. Numbers present in red exceed NSR significant emission rate thresholds.

Table 2. Estimated change in potential-to-emit (PTE) for co-located scenario at 4 biorefinery sizes

Bio-Oil Production Rate (barrels per day)	***1,400***	***2,700***	***4,200 (base case)***	***11,625***	***NSR Significant Emission Rate***
Number of U.S. Refineries with 5% FCCU capacity less than Bio-Oil Production Rate					
Out of 95	***32***	***51***	***73***	***95***	**--**
Annual Emissions (tons per year)					
PM	24	46	72	199	25
PM_{10}	8.0	15	24	67	15
$PM_{2.5}$	1.9	3.7	5.8	16	10
VOC	17	34	52	145	40
NO_x	30	58	90	249	40
CO	24	47	72	201	100
SO_2	2.5	4.8	7.5	21	40

For the NSR program, a PSD or NNSR major modification permit would be needed if the emissions of any regulated pollutant are above SER or NNSR major modification rates. Table 3 lists the permit ramifications and additional controls that the biorefinery may elect to install to avoid a PSD or NNSR major modification permit.

Table 3. NSR permit ramifications and additional control options to avoid major modification

Biorefinery size (barrels/day)	**Current NSR permit needed**	**Emission controls to avoid major modification permit**
1,400	Minor	Not applicable
2,700, 4200	PSD or major NNSR (PM, PM_{10}, and NO_x)	1. PM, PM_{10}: Paved roads for truck traffic and possible limit in production rate 2. NO_x: More efficient NO_x control device (selective catalytic reduction)
	PSD or major NNSR (VOC)	VOC: Reduce VOC emissions from storage tanks by routing it to a control device or capturing it via recovery system
11,625	Complex PSD or major NNSR (PM, PM_{10}, $PM_{2.5}$, VOC, NO_x, and CO)	No potentially and economically feasible control device would reduce emissions of all the pollutants to below SER values.

Additional emissions and permitting ramifications for the petroleum refinery co-processing bio-oil from an offsite facility

Table 4 reflects the additional emissions from the petroleum refinery due to process changes required for co-processing. It is assumed that the co-processing of 5% bio-oil would not cause an increase in emissions from the FCCU as the characteristics of the bio-oil are similar to VGO with lower concentrations of sulfur and chlorine. As shown in Table 4, VOC emissions from larger refineries (above 4,200 barrels per day) are estimated to exceed the SER limit. Additional emission controls could be available to further reduce the emissions to below the SER. For example, the petroleum refinery could avoid PSD and/or NNSR by installing a floating roof on the storage tank or routing the emissions to a control device such as an on-site incinerator, reducing the emissions by more than 90%.

Table 4. Additional emissions from the petroleum refinery co-processing bio-oil shipped from an offsite facility

Bio-Oil Production Rate (barrels per day)	*1,400*	*2,700*	*4,200 (base case)*	*11,625*	*NSR Significant Emission Rate*
Number of U.S. Refineries with 5% FCCU capacity					
Out of 95	***32***	***51***	***73***	***95***	--
Additional Emissions (tons per year)					
PM	2.3	4.4	6.8	19	25
PM_{10}	0.67	1.3	2	5.6	15
$PM_{2.5}$	0.07	0.13	0.2	0.56	10
VOC	18	30	51	133	40

Also, several federal regulations might apply to the new equipment and operation at the petroleum refinery that may require additional controls or work standards to meet the emission limitations, if applicable. Table 5 summarizes outcomes of the regulatory applicability for the new equipment at the petroleum refinery.

Table 5. Regulatory applicability for new equipment at the petroleum refinery

Equipment	Air Pollutants	NSPS & NESHAP That Could Apply	Applicability
FCCU, catalytic reforming units, sulfur recovery units, and miscellaneous process vents	VOC, HAP, CO, NO_x, H_2S, PM, PM_{10}, $PM_{2.5}$	NSPS Subpart J and Ja	Already applicable to individual equipment at refinery (no changes due to new storage tank)
		NESHAP Subpart CC, NESHAP Subpart UUU	Already applicable to the refinery (no changes due to new storage tank)
Storage tanks	VOC, HAP	NSPS Subpart Kb, NESHAP Subpart CC	Does not meet the vapor pressure threshold
Equipment Leaks	VOC, HAP	NSPS Subpart VVa	Does not meet SOCMI definition
		NESHAP Subpart CC (part 63)	Does not meet the total organic HAP requirement
		NESHAP Subpart J (part 61)	Does not meet benzene concentration requirement

SOCMI = synthetic organic chemical manufacturing industry

As shown in Table 5, the addition of new equipment due to process changes required for co-processing does not appear to trigger any additional federal regulations or emission limitations that could significantly alter the emissions of the petroleum refinery.

SUMMARY

We evaluate the potential air pollutant regulatory and permitting implications for co-processing partially upgraded bio-oil (5% by volume) in the petroleum refinery for two cases with and without co-locating with a bio-oil facility. We also analyze additional emission controls for the pollutants exceeding SER or NNSR major modification thresholds to avoid being subject to PSD and/or major NNSR permitting. Our results indicate that co-processing bio-oil shipped from an offsite facility would be a practical and more appealing approach as it does not significantly increase the emissions and trigger PSD permitting requirements. Also, feasible emission control options are available to avoid major modifications, though the costs of adopting these controls should be evaluated before making the final investment decision. Our analysis could help stakeholders make more informed decisions and help develop strategies to minimize permitting time and burdens.

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DISCLAIMER

REFERENCES

1. CARB (California Air Resource Board). *Co-processing of biogenic feedstocks in petroleum refineries*. 2017. See https://www.arb.ca.gov/fuels/lcfs/lcfs_meetings/020717_staffdiscussionpaper.pdf (accessed March 2018).

2. 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.

3. Stefanidis SD, Kalogiannis KG, Lappas AA. *Co-processing bio-oil in the refinery for drop-in biofuels via fluid catalytic cracking*. WIREs Energy Environ. **2017**.

4. Wang C, Li M, Fang Y. *Coprocessing of Catalytic-Pyrolysis-Derived Bio-Oil with VGO in a Pilot-Scale FCC Riser*. Ind Eng Chem Res. **2016**; 55(12):3525–34.

5. EPA. *New Source Review (NSR) permitting*. See http://www.epa.gov/nsr (accessed March 2018).

6. EPA. *Basic information about operating permits*. See https://www.epa.gov/title-v-operating-permits/basic-information-about-operating-permits (accessed March 2018).

7. Dutta, A; Sahir, AH; Tan, E; Humbird, D; Snowden-Swan, LJ; Meyer, PA; et al. *Process Design and Economics for the Conversion of Lignocellulosic Biomass to Hydrocarbon Fuels: Thermochemical Research Pathways with in Situ and Ex Situ Upgrading of Fast Pyrolysis Vapors*; Pacific Northwest National Laboratory (PNNL): Richland, WA; 2015; PNNL-23823.

8. Energy Information Administration (EIA). *Refinery Capacity Report*. See https://www.eia.gov/petroleum/refinerycapacity/table3.pdf (accessed March 2018).

9. EPA. *Emissions Factors & AP 42, Compilation of Air Pollutant Emission Factors*. 1995. See http://www3.epa.gov/ttn/chief/ap42/index.html#toc (accessed March 2018).

10. ASPEN. *Release 7.2, in AspenPlus2007*. Aspen Technology Inc.: Cambridge, MA; See www.aspentech.com (accessed March 2018).

11. EPA. *TANKS Emissions Estimation Software, Version 4.09D*. 2006. See http://www.epa.gov/ttnchie1/software/tanks/ (accessed March 2018).

12. EPA. *RACT/BACT/LAER Clearinghouse (RBLC)*. See http://cfpub.epa.gov/rblc/ (accessed March 2018).

13. EPA. *National Emission Standards for Hazardous Air Pollutants from Petroleum Refineries; Proposed Rule*. Federal Register Notice; 2007. See https://www.gpo.gov/fdsys/pkg/FR-2007-09-04/pdf/E7-17009.pdf (accessed March 2018).

14. Code of Federal Regulations. *NESHAP, 40 CFR 63 Subpart FFFF - Miscellaneous Organic Chemical Manufacturing*. 2003. See http://www.ecfr.gov/cgi-bin/text-idx?node=sp40.13.63.ffff (accessed March 2018).

KEYWORDS

Biorefinery, potential-to-emit, air permitting, bio-oil, co-processing, emission controls