

Air Pollutant Emissions and Regulatory Implications of a Biorefinery Producing Raw Bio-Oil

Preprint

Arpit Bhatt and Yimin Zhang

National Renewable Energy Laboratory

Presented at the 112th Annual Air and Waste Management Association Annual Conference Quebec City, Quebec June 25-28, 2019

NREL is a national laboratory of the U.S. Department of Energy Office of Energy Efficiency & Renewable Energy Operated by the Alliance for Sustainable Energy, LLC Conference Paper NREL/CP-6A20-73611 November 2019

This report is available at no cost from the National Renewable Energy Laboratory (NREL) at www.nrel.gov/publications.

Contract No. DE-AC36-08GO28308



Air Pollutant Emissions and Regulatory Implications of a Biorefinery Producing Raw Bio-Oil

Preprint

Arpit Bhatt and Yimin Zhang

National Renewable Energy Laboratory

Suggested Citation

Bhatt, Arpit and Yimin Zhang. 2019. *Air Pollutant Emissions and Regulatory Implications of a Biorefinery Producing Raw Bio-Oil: Preprint*. Golden, CO: National Renewable Energy Laboratory. NREL/ CP-6A20-73611. <u>https://www.nrel.gov/docs/fy20osti/73611.pdf</u>.

NREL is a national laboratory of the U.S. Department of Energy Office of Energy Efficiency & Renewable Energy Operated by the Alliance for Sustainable Energy, LLC Conference Paper NREL/CP-6A20-73611 November 2019

This report is available at no cost from the National Renewable Energy Laboratory (NREL) at www.nrel.gov/publications.

Contract No. DE-AC36-08GO28308

National Renewable Energy Laboratory 15013 Denver West Parkway Golden, CO 80401 303-275-3000 • www.nrel.gov

NOTICE

This work was authored by the National Renewable Energy Laboratory, operated by Alliance for Sustainable Energy, LLC, for the U.S. Department of Energy (DOE) under Contract No. DE-AC36-08GO28308. Funding provided by the U.S. Department of Energy Office of Energy Efficiency and Renewable Energy Bioenergy Technologies Office. The views expressed herein do not necessarily represent the views of the DOE or the U.S. Government. The U.S. Government retains and the publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for U.S. Government purposes.

This report is available at no cost from the National Renewable Energy Laboratory (NREL) at <u>www.nrel.gov/publications</u>.

U.S. Department of Energy (DOE) reports produced after 1991 and a growing number of pre-1991 documents are available free via <u>www.OSTI.gov</u>.

Cover Photos by Dennis Schroeder: (clockwise, left to right) NREL 51934, NREL 45897, NREL 42160, NREL 45891, NREL 48097, NREL 46526.

NREL prints on paper that contains recycled content.

INTRODUCTION

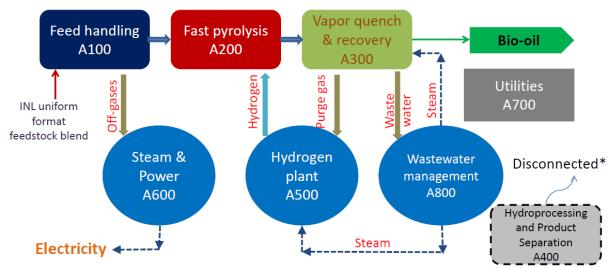
Pyrolysis oil, also referred to as bio-oil, has attracted considerable attention because of the high carbonaceous matter and high heating value compared to the original biomass before conversion.^{1–3} Utilizing the existing fossil fuel infrastructure by introducing raw bio-oil in the fluidized catalytic cracking (FCC) unit in petroleum refineries to produce renewable hydrocarbon fuels (i.e., repurposing existing assets) offers a promising opportunity to reduce the carbon intensity of transportation fuels and would present a relatively low capital requirement to existing facilities.^{1,4} However, a facility (biorefinery) producing raw bio-oil is considered a chemical process plant under the Clean Air Act (CAA)⁵ permitting program and is expected to emit air pollutants that could pose threats to the environment and public health. Based on the type and magnitude of the regulated pollutants emitted, the biorefinery may be subject to 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.^{6,7} This paper examines the potential regulatory implications (in terms of emissions and federal regulations) of a biorefinery producing raw bio-oil.

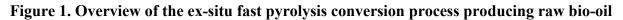
In this analysis, we examine the air pollutant emissions (preliminary potential to emit (PTE)) and evaluate the potential air pollutant regulatory and permitting implications for a biorefinery utilizing an ex situ fast pyrolysis process, with a design capacity of 2,000 dry metric tons of biomass per day to produce 4,200 barrels of raw bio-oil.⁸ The raw bio-oil produced from the biorefinery can be blended with petroleum-based intermediates (vacuum gas oil) in the FCC units of existing petroleum refineries to produce gasoline and diesel blendstocks with renewable content. We also discuss selected emissions control technologies, which could be used to further reduce potential emissions (alternative PTE) and help biorefineries avoid being subject to the major source permitting requirements (e.g., prevention of significant deterioration (PSD)) if desired. This analysis is expected to provide insights for new bio-oil project developers to identify opportunities to mitigate emissions and develop strategies to overcome challenges and risks associated with air permitting. Our previous analysis investigated permitting ramifications of co-processing partially upgraded bio-oil in petroleum refineries while this analysis looks into regulations and permitting classification for a biorefinery producing raw bio-oil.

METHODS

Overview of process design

The ex-situ fast pyrolysis process to produce raw 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 (Figure 1). Dried and heated biomass is fed to the non-catalytic fast pyrolysis reactor to produce pyrolysis vapors with low oxygen content. Char is separated using cyclones and sent back to char combustor for use as a heat source for pyrolyzer. The vapors are quenched in the series of absorbers to separate the organic fraction (raw bio-oil) from the non-condensable gases. The raw 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 raw bio-oil as a final product and does not include any vapor upgrading and hydrotreating and hydrocracking operations.





To evaluate the potential-to-emit for ex-situ fast pyrolysis biorefinery, we carry out of series of steps outlined below:

Step 1: Identification of air pollutants

To determine pollutants likely to be emitted from the biorefinery, we analyze each unit operation to identify the emitting sources. We use the U.S. Environmental Protection Agency's (EPA) guidelines (e.g., EPA's Compilation of Air Pollution Emission Factors [AP-42]),⁹ conduct material balances using process engineering models (such as Aspen Plus), and examine air permits for analogous operations and equipment.

Step 2: Applicability of federal regulations

Based on the specific unit operation and equipment design along with the type of pollutants expected to be emitted, we review the applicability criteria for each federal standard to determine whether a facility or equipment is subject to it. Two federal standards that regulate the air pollutants from stationary sources are NSPS and NESHAP.

Step 3: Estimation of the PTE

We estimate the PTE using published emission factors (e.g., AP-42 emission factor database) and material balance method. We consider the maximum capacity of unit operation/equipment, worst-case emissions (in case of multiple fuel sources), physical and operational design limitations, and federally enforceable limits (e.g., from applicable federal regulations). We also assume that the air emission control equipment planned in the biorefinery design is included in the air permit issued by state and local permitting agencies under EPA-approved programs; therefore, the control equipment is considered federally enforceable.

INL = Idaho National Laboratory

Step 4: Permitting classification

The NSR program requires a facility to apply for a construction permit before a project is built or modified. If a source exceeds an applicable major source threshold for any regulated air pollutants, it will be classified as a major source. We compare the estimated PTE for each regulated air pollutant with the major source threshold to determine the permitting classification for the biorefinery design. In general, major source thresholds for pollutants emitted from a chemical manufacturing plant (such as the biorefinery) are 100 tons per year (tpy) for criteria pollutants, 10 tpy for any single hazardous air pollutant (HAP) or 25 tpy for any combination of HAPs.

Because biorefinery developers would prefer to avoid being subject to major source permitting, we examine selected controls technologies that could potentially allow the facility to reduce emissions to below major source thresholds. We use EPA's Reasonably Available Control Technology (RACT)/Best Available Control Technology (BACT)/Lowest Achievable Emission Rate (LAER) Clearinghouse database¹⁰ and air permit applications of similar processes to identify the potential emission controls. We then assume those controls to be a part of the conversion process and use the emission reduction efficiencies from published literature (e.g., EPA's air pollution control technology factsheets) to update the PTE estimates (referred to as alternative PTE here) to determine whether these controls could help the biorefinery achieve minor source classification.

RESULTS

Identification of potential air pollutants

Table 1 shows the types of air pollutants expected to be emitted from ex-situ fast pyrolysis biorefinery including particulate matter (PM) (and PM with less than or equal to 2.5 micrometers in diameter $[PM_{2.5}]$, PM with less than or equal to 10 micrometers in diameter $[PM_{10}]$), volatile organic compounds (VOC), nitrogen oxides (NO_x), sulfur dioxide (SO₂), carbon monoxide (CO), lead, and HAPs (e.g., benzene, formaldehyde). Because a biorefinery is considered a chemical manufacturing plant, we also estimate fugitive emissions in the form of equipment leaks and truck traffic for inclusion in the PTE estimates.

Plant Area	Equipment	Air Pollutants	
Feed Handling & Drying	Biomass feedstock transfer and storage	PM, PM ₁₀ , PM _{2.5}	
	Dryer	PM, PM ₁₀ , PM _{2.5} , VOC, HAP	
Ex Situ Non-Catalytic Fast Pyrolysis	Char combustor	PM, PM ₁₀ , PM _{2.5} , SO ₂ , VOC, CO ₂	
	Ash and sand handling operations	PM, PM ₁₀ , PM _{2.5}	
	Leaking equipment	VOC, HAP	
Pyrolysis Vapor Quench and Product Recovery	Leaking equipment VOC, HAP		
Hydrogen Plant	Methane reformer	PM, PM ₁₀ , PM _{2.5} , NO _x , SO ₂ , CO, CO ₂ , VOC, HAP	
	Leaking equipment	VOC, HAP	
Wastewater Management & Recycle	Aqueous regenerative thermal oxidizer	CO ₂ , VOC, HAP	
	RO & Clarifier	VOC, HAP	
Storage and Transfer	Product storage tanks	VOC, HAP	
	Equipment for loading products	VOC, HAP	
Utilities	Cooling tower	PM, PM ₁₀ , PM _{2.5} , VOC, HAP	
	Emergency fire pump	PM, PM ₁₀ , PM _{2.5} , NO _x , SO ₂ , CO, CO ₂ , VOC, HAP	
	Emergency generator	PM, PM ₁₀ , PM _{2.5} , NO _x , SO ₂ , CO, CO ₂ , VOC, HAP	
Truck Traffic	Dust from trucks hauling feedstock, other raw materials, waste, and product	PM, PM ₁₀ , PM _{2.5}	

Table 1. Air pollutants likely to be emitted from an ex-situ fast pyrolysis biorefinery

Potentially applicable regulations and preliminary potential to emit

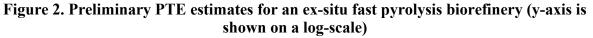
The federal regulations potentially applicable to the ex-situ fast pyrolysis biorefinery are listed in Table 2 below.

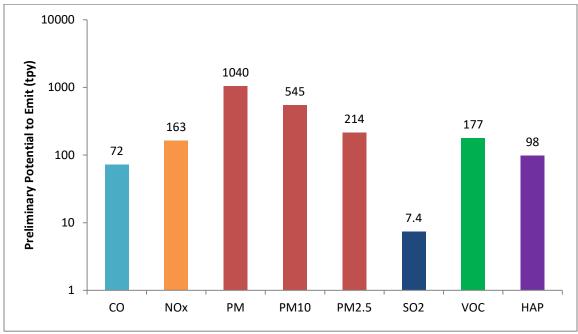
Table 2. Federal	regulations potenti	ally applicable to an	ex-situ fast pyro	olvsis biorefinerv
	- Summons potenti	my approact to an		, , , , , , , , , , , , , , , , , , ,

Potential Federal Regulations		
If facility is a major source of HAP, NESHAP Subpart FFFF applies		
or		
If facility is an area source of HAP, NESHAP Subpart VVVVVV applies		
Only if facility is a major source of HAP and meets the applicability criteria, NESHAP Subpart DDDDD applies		
NSPS Subpart IIII		
NESHAP Subpart ZZZZ		
If facility is a major source of HAP, NESHAP Subpart FFFF applies		
or If facility is an area source of HAP: NESHAP Subpart VVVVVV applies		

NSPS = New Source Performance Standards, NESHAP = National Emission Standards for Hazardous Air Pollutants

Based on the design and process characteristics, the emissions from an ex-situ biorefinery are estimated to be above the major source threshold for several pollutants. Therefore, NESHAP (40 CFR 63) Subpart FFFF applies to the whole biorefinery along with other regulations as shown in Table 2. We then include additional control options (in the form of control technology and monitoring requirements) to the dryer, cooling tower, and equipment leaks under NESHAP, Subpart FFFF (see Fig. 3 for emission estimates) to meet the regulatory limitations.





Notes:

1. Assume 98% reduction of HAPs from dryer under NESHAP, Subpart FFFF

2. Assume high efficiency drift eliminators and monitoring requirements for cooling towers for reducing PM and HAP emissions, respectively, under NESHAP, Subpart FFFF.

3. Assume a quarterly monitoring system for equipment leaks to reduce HAP emissions under NESHAP, Subpart FFFF.

Preliminary permitting classification

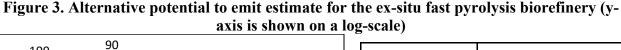
As shown in Figure 2, the estimated preliminary PTE of several regulated pollutants (PM, NO_x, VOC, and HAP) exceeds the major source thresholds. Thus, the ex-situ fast pyrolysis biorefinery would likely be subject to the major source permitting classification. In addition, the biorefinery would also be subject to Title V permitting program as the overall HAP emissions exceed the major source threshold value (i.e., 25 tons per year).

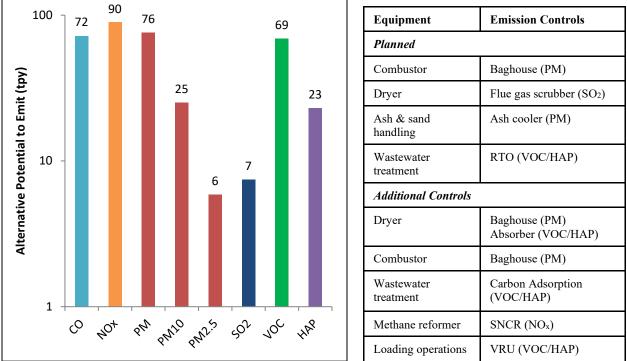
Emission reduction through control technologies (alternative potential to emit)

As described previously, if a facility prefers avoiding being subject to major source permitting requirements, it could take a step further to identify and adopt additional emission control technologies that may reduce emissions below major source thresholds (alternative PTE). For the ex-situ biorefinery, the dryer and char combustor are the primary contributor to PM emissions,

wastewater treatment is a primary contributor of VOC and HAP emissions, and the methane reformer is responsible for majority of the NO_x emissions. If a baghouse is assumed to be utilized to reduce PM emissions from the dryer, char combustor and catalyst regenerator along with a selective non-catalytic reduction (SNCR) to reduce NO_x emissions from the methane reformer, the facility-wide PTE for PM (including $PM_{2.5}$ and PM_{10}) and NO_x could be reduced to below the 100 tpy major source threshold.^{12,11}

In addition, the current ex-situ design utilizes a regenerative thermal oxidizer (RTO) to reduce 98% of the organic species from the wastewater management area. However, information on the specific organic species is unavailable. Without such information, it is difficult to suggest the most efficient emission controls to reduce the specific VOC and HAP species present in the wastewater and likely emitted into the air. However, we assume that a carbon adsorption system would be able to reduce VOC and HAP emissions by 95% from wastewater¹² along with a vapor recovery unit to reduce 90% of VOC and HAP emissions from loading operations.¹³ This would help the biorefinery achieve minor source classification (reduce emissions below 100 tpy for VOC and 25 tpy for HAP). Figure 3 shows the modeled alternative PTE after additional controls.





SUMMARY

We evaluated the potential air pollutant regulatory and permitting implications for a 2000 dry metric ton per day biorefinery producing raw bio-oil via ex-situ fast pyrolysis. We also analyzed an alternative set of PTE by identifying and adopting additional emission controls to reduce regulated air pollutants to assess the feasibility of avoiding being subject to major source air permitting requirements under the NSR and Title V permitting programs. Our preliminary results

indicate that the ex-situ biorefinery with planned emission controls would be classified as a major source under the NSR permitting program. However, feasible emission control options are available to avoid major source permitting, though the costs of adopting these controls should be evaluated before making the final investment decision. Our analysis provides insights into the potential challenges and risks associated with air permitting, which are often overlooked for the deployment of new technologies. Our analysis could help stakeholders make more informed decisions and help develop strategies to minimize permitting time and risks.

ACKNOWLEDGEMENTS

This work was authored by Alliance for Sustainable Energy, LLC, the Manager and Operator of the National Renewable Energy Laboratory for the U.S. Department of Energy (DOE) under Contract No. DE-AC36-08GO28308. Funding provided by U.S. Department of Energy Office of Energy Efficiency and Renewable Energy Bioenergy Technologies Office. The views expressed in the article do not necessarily represent the views of the DOE or the U.S. Government. The U.S. Government retains and the publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for U.S. Government purposes.

DISCLAIMER

The views and opinions of the authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights.

REFERENCES

- 1. EPA. *Renewable Fuel Standard Program (RFS2) Regulatory Impact Analysis,* 2010; EPA-420-R-10-006. See http://www3.epa.gov/otaq/renewablefuels/420r10006.pdf (accessed February 2017).
- BETO (U.S. Department of Energy Bioenergy Technologies Office). *Bioenergy Technologies Office, multi-year program plan*, 2016; See http://www.energy.gov/sites/prod/files/2016/07/f33/mypp_march2016.pdf. Office of Energy Efficiency and Renewable Energy: Washington, DC.
- 3. U.S. Code Sec. 7401. *Clean Air Act, Title 1 Air Pollution Prevention and Control*, Congressional findings and declaration of purpose. See https://www.gpo.gov/fdsys/pkg/USCODE-2013-title42/html/USCODE-2013-title42chap85-subchapI-partA-sec7401.htm (accessed February 2017).
- Zhang, Y; Bhatt, A; Heath, G; Thomas, M; Renzaglia, J;. Federal Air Pollutant Emission Regulations and Preliminary Estimates of Potential-to-Emit from Biorefineries, Pathway #1: Dilute-Acid and Enzymatic Deconstruction of Biomass-to-Sugars and Biological Conversion of Sugars-to-Hydrocarbons; National Renewable Energy Laboratory (NREL): Golden, CO; 2016; NREL/TP-6A20-62547.

- 5. Bhatt, A; Zhang, Y; Heath, G; Thomas, M; Renzaglia, J. Federal air pollutant emission regulations and preliminary estimates of potential-to-emit from biorefineries, Pathway #2: Conversion of Lignocellulosic Biomass to Hydrocarbon Fuels: Fast Pyrolysis and Hydrotreating Bio-oil Pathway; National Renewable Energy Laboratory (NREL): Golden, CO, 2017; NREL/TP-6A20-67333.
- 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.
- 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; 2013; PNNL-23053; NREL/TP-5100-61178.
- 8. Pinho, A de R; de Almeida, MBB; Mendes, FL; Ximenes, VL; Casavechia, LC;. *Coprocessing raw bio-oil and gasoil in an FCC Unit*. Fuel Process Technol. **2015**, 131, 159–66.
- 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 February 2017).
- 10. EPA. *RACT/BACT/LAER Clearinghouse (RBLC)*. See http://cfpub.epa.gov/rblc/ (accessed February 2017).
- 11. EPA. *Air Pollution Control Technology Fact Sheet*, 2003; EPA-452/F-03-034. See http://www.epa.gov/ttn/catc/dir1/ffdg.pdf (accessed February 2017).
- 12. EPA. *Air Pollution Control Technology Fact Sheet*, 2003; EPA-452/F-03-025. See http://www.epa.gov/ttnchie1/mkb/documents/ff-pulse.pdf (accessed February 2017).
- 13. EPA. *Air Pollution Control Technology Fact Sheet*, 2003; EPA-452/F-03-031. See http://www.epa.gov/ttncatc1/dir1/fsncr.pdf (accessed February 2017).

KEYWORDS

Biorefinery, potential-to-emit, permitting, bio-oil, emission controls, federal regulation