

COMPARATIVE TECHNO-ECONOMIC ANALYSIS AND LIFE CYCLE ASSESSMENT OF PRODUCING HIGH-VALUE CHEMICALS AND FUELS FROM WASTE PLASTIC VIA CONVENTIONAL PYROLYSIS AND THERMAL OXO-DEGRADATION.

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Abstract

The rapid rise in global plastic production in recent decades has resulted in a massive generation of plastic waste. Over 75% of the plastic waste generated in the United States was sent to landfill, with a meager 8.7% recycled. Plastics are a valuable feedstock for platform chemicals and fuels. Chemical upcycling of waste High-Density Polyethylene (HDPE) is gaining more attention as a potentially feasible and environmentally friendly plastic waste management technology. Conventional pyrolysis (CPY) and thermal oxo-degradation (TOD) are two chemical upcycling technologies actively researched for decomposing waste HDPE into valuable chemicals and fuels. However, there are few studies on these technologies' techno-economic analysis (TEA) and life cycle assessment (LCA) for converting waste HDPE to valuable products. This study conducts a comparative TEA and LCA on the thermochemical decomposition of waste HDPE to produce gaseous (ethylene and propylene) and liquid products (naphtha, diesel, and wax) by CPY and TOD.

The study elucidates and compares the impact of hydrocracking longer-chain hydrocarbons to produce more valuable products on the TEA and LCA. The TEA showed that the fixed capital investment could range from \$32.5 million for TOD without hydrocracking to \$244 million for CPY with hydrocracking scenarios. Annual revenues range from \$28.1 to \$71.5 million in favor of scenarios with hydrocracking. However, the net present value ranges from \$1.4 to 265.8 million in favor of scenarios without hydrocracking. Sensitivity analysis showed that fixed capital cost, facility capacity, and product prices have the biggest impact on the process economics of the facilities, while utilities and waste transportation to refineries have the biggest impact on environmental impacts. The LCA showed that primary products from scenarios without hydrocracking can be more environmentally friendly than virgin products from petroleum processes. However, TOD and CPY with hydrocracking primary products have more emissions than virgin products.

Introduction

The rapid rise in global plastic production in recent decades due to its low price, versatility, and relevance in almost every field of human activity has led to a growing problem of plastic waste generation and management^{1,2}. Global annual production of plastics rose from 1.5 million metric tonnes (MT) in 1950 to 390.7 million MT in 2021, with 18% originating in the United States^{3,4}. As expected, global plastic waste generation has also increased to about 400 million tonnes annually⁵. Of the 35.7 million tons of plastic waste generated in the United States in 2018, only 8.7% were recycled, 75.6% sent to landfills, and the rest combusted with energy recovery⁶. Waste plastics can be a significant problem for landfills because, unlike organic waste, plastics are non-biodegradable and can emit harmful chemicals that pose environmental and health threats. Also, waste plastics take up valuable space and contribute to filling landfills faster².

Chemical recycling of waste plastics has been identified as one of the viable ways to combat waste plastics challenges as it involves breaking waste plastics into their monomers or valuable chemical feedstocks through thermal, chemical, or enzymatic degradation². Unlike mechanical recycling methods that degrade the polymer properties of plastics, chemical recycling can create new products with similar characteristics to virgin products². Among chemical recycling technologies, the thermal decomposition of waste plastics has been identified as one of the most viable pathways for upcycling waste plastics due to plastics' high heating value and ability to be decomposed to monomers and shorter chain hydrocarbons that can potentially replace chemicals and transportation fuel produced from fossil sources². Various thermochemical technologies like pyrolysis, gasification, and hydrothermal liquefaction have been investigated, and some industrial plants are already in production^{2,7}. Conventional pyrolysis (CPY), which is the thermal decomposition of feedstocks at high temperatures (typically between 300 °C and 700 °C) in the absence of oxygen, has been widely studied as a thermochemical pathway to break down waste plastics at high temperatures into monomers, polymerized to create plastics⁸⁻¹⁰. Thermal oxo-degradation (TOD) is a similar technology to pyrolysis, which has been studied and shown to reduce the energy requirements of conventional pyrolysis by the addition of oxygen into the reactor to allow for partial oxidation of the pyrolysis products to provide the pyrolysis process heat¹¹. Depending on the process temperatures, residence time, and presence of oxygen or no oxygen in the reactor, waste plastics pyrolysis can yield products ranging from gaseous products (ethylene, propylene, butene) to valuable hydrocarbons like naphtha range, diesel range, and long-chain hydrocarbons like wax².

Few research studies have examined the techno-economic analysis and life cycle assessment of chemically recycling waste plastics via pyrolysis¹²⁻¹⁴. Fivga & Dimitriou¹² and Sahu et al.¹⁴ have shown that the pyrolysis of waste plastics to produce liquid fuel can be economically feasible at a large scale (greater than 7012 MT/year). Other studies went further to investigate the production of multiple products from the pyrolysis of waste plastics by including more product upgrading steps after the pyrolysis process¹⁵⁻¹⁷. Gracida-Alvarez et al.¹⁷ showed that on a scale of 500 MT/day, the production of multiple products from the pyrolysis of waste HDPE can result in a net present value of \$367 and \$383 million. All these studies have shown that pyrolysis of waste plastics can be a viable pathway to recycle waste plastics. Gracida Alvarez et al.¹⁸ also analyzed the pyrolysis system's carbon footprint using the system expansion method to allocate emission burdens to each product. They showed that the greenhouse gas (GHG) emissions associated with ethylene, propylene, and aromatics mixture from their

scenarios are lower than from fossil sources, but naphtha and diesel range products do not compare favorably with those from fossil sources ¹⁸.

Having established from the literature that waste plastics pyrolysis can be an economically viable and potentially environmentally friendly pathway to recycle waste plastics, we intend to compare the economic feasibility of pyrolysis and TOD. To the best of our knowledge, no study has investigated the economic feasibility, the life cycle assessment of thermal oxo-degradation, or compared the technology to conventional pyrolysis of waste plastics. Some studies have compared various chemical recycling technologies' economics and environmental impacts for converting waste plastics into value-added products ^{13,19}. Hernández et al. have compared the TEA and LCA of Pyrolysis, hydrogenolysis, gasification, hydrocracking, and hydrothermal liquefaction of low-density polyethylene waste (LDPE) to produce different products. The study found the pyrolysis of LDPE to olefins, followed by the conversion to lubricant oil, to be the most profitable thermochemical upcycling technology for LDPE with a return on investment (ROI) between 13 and 17% ¹⁹. However, the study did not include TOD.

This study aims to compare the thermochemical conversion of waste plastics to multiple value-added products via conventional pyrolysis and thermal oxo-degradation. This study investigates the economic feasibility and environmental impacts of producing ethylene, propylene, naphtha, diesel, and wax from conventional pyrolysis and thermal oxo-degradation. The study also considers the impacts of further upgrading the pyrolysis products to more valuable products via hydrocracking on the economics and environmental burdens of the technology.

Methodology

The study focuses on the thermal decomposition of HDPE waste into gaseous and liquid products under six different scenarios to produce ethylene, propylene, naphtha range, diesel range, and waxes. From now on, naphtha range and diesel range products will be referred to as naphtha and diesel, respectively. The six scenarios include four scenarios using CPY and two scenarios using the TOD technology. For the CPY scenarios, we considered one-second- and 20-second residence times and both scenarios with hydrocracking and without hydrocracking. For scenarios with TOD technology, we considered one-second residence time with and without hydrocracking. Therefore, the six scenarios are one-second residence time conventional pyrolysis without product upgrading (CPY), one-second residence time conventional pyrolysis with hydrocracking (CPY-HC), 20-second residence time conventional pyrolysis without hydrocracking (HRT), 20-seconds residence time conventional pyrolysis with hydrocracking (HRT-HC), thermal oxo-degradation without hydrocracking (TOD) and thermal oxo-degradation with hydrocracking (TOD-HC) (see Table 1).

Table 1. Process Parameters of the six Scenarios considered in this study.

Technology	Residence time (Secs)	Biomass to Air ratio	Hydrocracking
TOD - HC	1	93:7	Yes
TOD	1	93:7	No
CPY-HC	1	100:0	Yes
CPY	1	100:0	No
HRT-HC	20	100:0	Yes
HRT	20	100:0	No

Overview of the Process Model

The conceptual refinery design for all scenarios was developed in BioSTEAM 2.35.0²⁰ to process 250 tonnes of waste HDPE per day using common equipment found in pyrolysis refineries. We settled for a 250 tonnes per day (TPD) capacity in line with ~300 TPD pyrolysis plants in literature and under construction¹³. The mass and energy balance from the conceptual process model is used for economic analysis and life cycle assessment.

The refinery consists of four major processing steps: the feed pretreatment and pyrolysis section, the product fractionation section, the hydrogen production section, and a hydrocracking section for scenarios that include pyrolysis oil upgrading. For scenarios without hydrocracking, the pyrolysis products go to product fractionation, where ethylene, propylene, naphtha, diesel, and waxes are collected as final products. For scenarios with hydrocracking, the longer chain hydrocarbons are cracked into lighter hydrocarbons in the hydrocracking section. For product fractionation, C4 – C10 hydrocarbons are collected as naphtha, C11 – C20 hydrocarbons are collected as diesel, and hydrocarbons with more than 20 carbon molecules are collected as wax. The Soave Redlich Kwong (SRK) equation of state predicted the vapor–liquid equilibrium for the refinery. Pyrolysis process yields for CPY and TOD, shown in Table S2 in supporting information (SI), were obtained from ISU's experimental group, and process yields for HRT were obtained from the pyrolysis group at the University of Wisconsin (See Table S2 in SI). Figure 1 shows the process flow diagram (PFD) of the conventional pyrolysis with hydrocracking scenarios. Figure S1-4 in the SI shows the process flow diagram for thermal oxo-degradation with and without hydrocracking and conventional pyrolysis scenarios with and without hydrocracking. The four sections modeled in the processes are discussed below.

Pyrolysis

The process model begins with feedstock pretreatment, where HDPE is reduced in size in a hammer mill that requires 300 kWh/tonne of electricity¹⁷. The granulated plastics from the hammer mill are then fed into a fluidized bed reactor operating at 600°C. The waste HDPE is pyrolyzed using sand and nitrogen as heating and fluidizing agents. For CPY and HRT, the sand is heated to about 1200°C in a sand furnace before being fed into the pyrolysis reactor as heating agents. The pyrolysis vapors are sent to a cyclone that removes solids, including char, solid HDPE, sand, and any other solid present in the pyrolysis vapor stream. For conventional pyrolysis, we assumed that the solids from the cyclone and the non-condensable gases (NCG) collected downstream are recirculated back to the combustion chamber to supplement natural gas in providing process heat. However, for TOD, the waste HDPE is fed into the pyrolysis reactor along with oxygen at a volume equivalent ratio of 93:7 (HDPE: Oxygen). Oxygen is provided in the reactor to allow for partial oxidation of the pyrolysis products to provide process heat for pyrolysis. The TOD vapor is sent to a cyclone, where solids in the vapor are collected and recirculated to the pyrolyzer. The process heat produced from the partial oxidation of the pyrolysis process is supplemented by unrecovered NCGs downstream, as shown in the PFD (Figures S3 and S4 in SI).

Product fractionation

For all scenarios, the pyrolysis vapor from the cyclones is cooled and condensed at 15°C to yield light gases and liquid pyrolysis oil. The heavy oil is sent to a flash separator operating at 370 °C to separate the waxes from the naphtha and diesel in the heavy oil stream. The light gases, which consist of C1 to C4 hydrocarbons, are further cooled to -136°C, cryogenic temperatures and compressed to 7 bars through a series of refrigeration cycles, compressors, and condensers to separate C2 to C4 gases. As

stated earlier, the rest of the NCG is recycled to provide process heat in the pyrolysis section for all scenarios. The C2 – C4 gases are heated to about 2°C and compressed to 25 bars for all scenarios. The stream is then passed through a de-ethanizer column to collect ethylene. The distillate from the de-ethanizer is further processed in an ethylene fractionator to separate the ethylene from other gases present in the stream. The other gases, which comprise mainly CO₂ and propylene, are sent to the pyrolysis reactor to aid fluidization. The bottom of the de-ethanizer is sent to a depropanizer, where propylene is separated from heavier hydrocarbons. The propylene in the distillate is further purified by passing the stream through a propylene fractionator. The bottoms from the propylene fractionator are also sent to the pyrolyzer to aid fluidization and to be combusted to provide process heat. The bottoms of the depropanizer, which majorly contain C₄ hydrocarbons, are sent with the light oil from the flash separator pyrolysis liquid to a de-butenizer, where butene is recovered in the distillate. The bottoms of the debutanizer are sent to a naphtha splitter to collect the naphtha and a diesel splitter to recover the diesel.

The diesel splitter and the flash separator bottoms are collected as wax for scenarios without hydrocracking. However, for scenarios with hydrocracking, the bottoms are sent to the hydrocracking unit, where the wax is cracked to naphtha and diesel.

Hydrocracking

Hydrocracking is a refining process that involves breaking down long-chain hydrocarbons into shorter-chain hydrocarbons by treating them with hydrogen in the presence of a catalyst at high temperature and high pressure. The bottoms from the diesel splitter and flash operator are fed to the hydrocracking unit, which is broken down into shorter-chain hydrocarbons. The hydrocracking product includes naphtha and diesel. We assumed that the oxygenated products in the pyrolysis products are less than 3%, as provided by the experimental groups (See Table S2 in SI). Hence, we assumed that the oxygenated compounds are negligible and that hydrotreating is not required. Hydrocracking is a mature technology used in various previous studies^{21,22} that is not modeled explicitly in this study. The hydrogen required for the hydrocracking process is purchased.

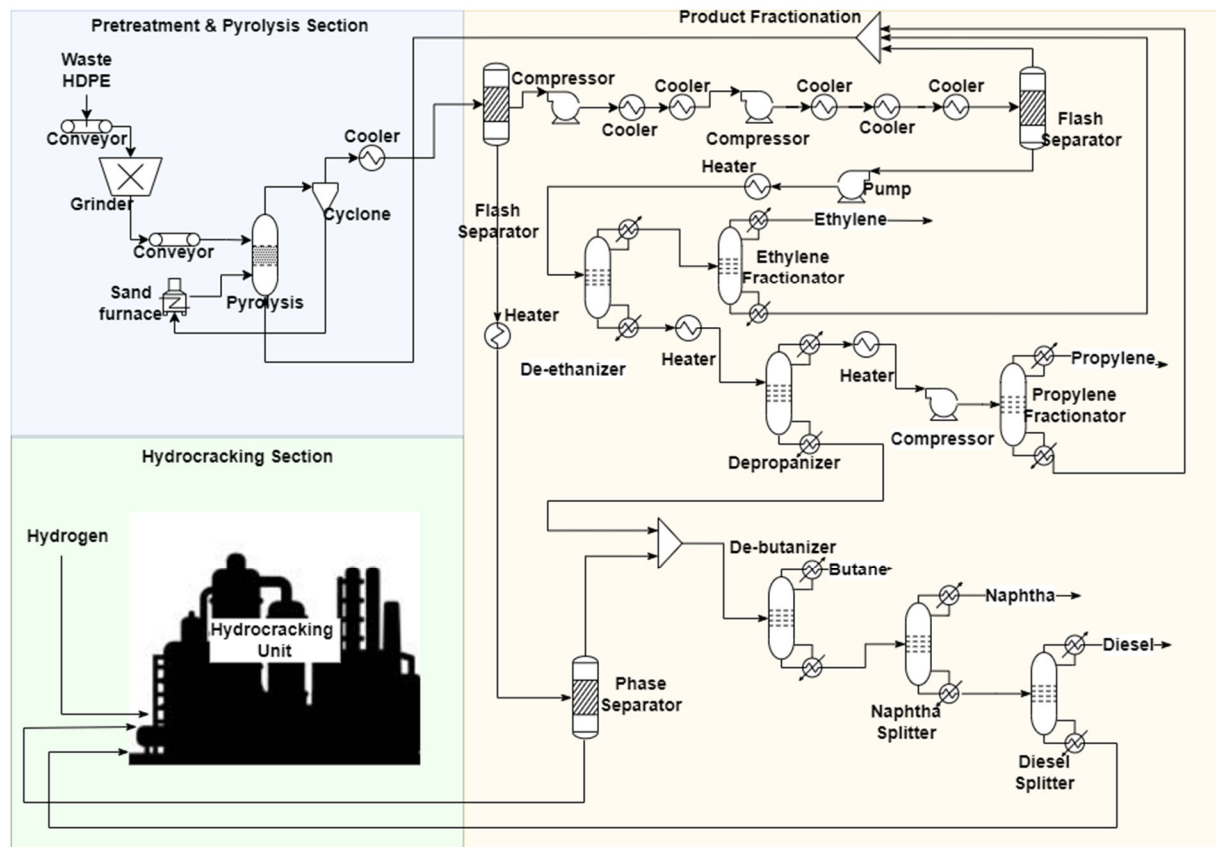


Figure 1. Process flow diagram for scenarios with conventional pyrolysis and hydrocracking.

Techno-Economic Analysis

This study utilizes techno-economic analysis TEA to estimate the economic feasibility of all six scenarios in this study to compare the economic feasibilities of chemically upcycling waste HDPE to value-added products via the six scenarios discussed earlier. The mass and energy balance from the BioSTEAM process models was used for capital and operating cost estimates. The study employs the discounted cash flow rate of return (DCFROR) commonly used in similar studies^{13,19,21} to estimate each scenario's NPV. The NPV was selected as the economic indicator to compare the scenarios because it allows for straightforward economic feasibility estimates and multiple technologies comparison for multi-product facilities. In other to compare the products with current substitutes from petroleum processes, the product with the largest fraction in the product steam was selected as the primary product, and the DCFROR was utilized to estimate the minimum selling price of the primary product of each scenario by treating other products as co-products.

Financial Assumptions

The plant is designed based on the n^{th} plant assumption, which implies that the technology is fully matured, and similar technologies are already used in the industry^{23,24}. The financial assumptions made in this study follow closely with assumptions made in other TEA studies where the n^{th} plant assumptions are used^{17,25}. The study assumes that 40% of the facilities expenses are covered by equity while 60% will be financed at a 10% interest rate and a ten-year repayment period. In estimating the NPV of the refineries, the study assumes a 10% IRR over a 20-year plant life. The study assumed a

construction period of three years and a start-up time of six months. All costs in this analysis were adjusted to 2020 rolling dollars. Table 2 shows a list of the financial assumptions made in the study.

Table 2. Financial assumptions for the techno-economic analysis.

Parameters	Financial assumptions
Equity	40%
Financing interest rate	10%
Term for debt financing	10 years
Income tax rate	21%
Internal rate of return	10%
Plant-life	20 years
Construction period	3 years
Depreciation period	7 years MACRS schedule
Working capital	20% of Fixed capital cost
Project contingency	10% of Fixed capital cost
Plant salvage value	\$0
Start-up time	0.5 years
Revenue and cost during start-up	50% of normal revenue
	75% of the normal variable cost
	100% of fixed cost
Electricity price	6.56 cents/kWh

Capital and Operating Cost

Fixed Capital investment (FCI) refers to the initial investment required to set up the facility. Capital cost includes engineering design, equipment, building, and other costs associated with licenses and permits. The total installed equipment cost for different scenarios is calculated based on the equipment required. The cost of equipment depends on the type and capacity of the equipment. The mass and energy balance from the process model was used to determine the capacity of the equipment. The data source for equipment cost varies with the type of equipment. The cost of equipment used in the study was based on the literature^{17,22}. The cost of heat exchangers, compressors, and distillation columns are taken from BioSTEAM. The study employs Equation 1 using exponential factors to adjust the equipment cost taken from the literature from the original capacity reported in the literature to the capacity required in the study.

$$Cost_{new} = Cost_{base} * \left(\frac{Capacity_{new}}{Capacity_{base}} \right)^n \quad \text{Equation 1}$$

Where $Cost_{new}$ is the cost of the equipment at new capacity and $Cost_{base}$ is the original cost of the equipment reported in the literature. $Capacity_{base}$ is the original capacity reported in the literature, while $Capacity_{new}$ is the capacity of the equipment used in the study, and n is the exponential factor that can vary from 0.6 to 1 depending on the equipment. The study also employed the chemical engineering plant cost index (CEPCI) to update the equipment cost from the time of design to the year 2020 using Equation 2

$$Cost_c = Cost_b \cdot \frac{CEPCI_c}{CEPCI_b} \quad \text{Equation 2}$$

Where $CEPCI_c$ and $CEPCI_b$ are the CEPCI at the current year and the year, the equipment was designed, respectively, and $Cost_c$ and $Cost_b$ is the cost of the equipment at the current year and the year of design, respectively.

Operating cost is the ongoing expenses required to keep the facility running. Operating cost includes raw material cost, labor cost, overhead cost, utility cost, and waste disposal. The cost of waste HDPE was taken from ¹⁷. Gracida-Alvarez et al. (2019) estimated the cost of waste HDPE as the difference between the average cost of processing waste HDPE in the material recovery facility and the tipping fee received at the reception. The market prices of ethylene, propylene, naphtha, and diesel were taken from Gracida-Alvarez et al. (2019). The prices of natural gas and hydrocracking catalyst market information. Due to the low quality of wax produced in these processes, we assumed the wax price to be 30 cents per kg. We believe the wax will undergo significant processing to attain the purity and quality of paraffin wax in the market. Table 3 shows the operating cost price assumptions.

Table 3. Operating cost assumptions of the techno-economic analysis.

Parameters	Price	unit	Source
HDPE	25.05	\$/MT	17
Natural Gas	5.81	\$/scf	23
Hydrocracking Catalyst	42.51	\$/kg	23
Electricity	7.01	¢/kwh	23
Ethylene	0.61	\$/kg	17
Propylene	0.97	\$/kg	17
Butene	1.27	\$/kg	13
Naphtha	0.86	\$/kg	17
Diesel	0.84	\$/kg	17
Wax	0.30	\$/kg	

Finally, sensitivity analysis was conducted to evaluate the impact of key process parameters on the NPV of the six scenarios. Sensitivity analysis is used to estimate the impact of a 20% change in the baseline prices of product yields, IRR, FCI, feedstock cost, and hydrocracking catalyst, where applicable, on the net present value of the facility. The variables selected for the sensitivity analysis are in line with similar studies in literature ^{23,26}.

Life Cycle Analysis

Life cycle assessment (LCA) is a widely accepted methodology for estimating a system or product's health and environmental impact. LCA entails the examination of different phases a product undergoes, starting with the acquisition of raw materials, followed by manufacturing, distribution, utilization, and finally, the stage of disposal or recycling. This study employed LCA to evaluate the health and environmental impacts of producing value-added products from chemically upcycling waste HDPE via the six scenarios. This study adheres to the ISO 14040 and 14044 frameworks ²⁷ which provide standardized guidelines for conducting LCA studies.

Table 4. Emission factors for life cycle analysis compiled in OpenLCA ³² using USLCI database ³¹

Emission Source	100- Year GWP (kg CO ₂ -Eq)	Unit
Diesel	4423.2	per cubic meter
Electricity	1.8E-1	per kWh
Gasoline	2339.1	per cubic meter
Hydrogen	9.3	per kg
Natural Gas for heat	6.9E-2	per MJ
Transport	1.7E-1	per (tonne * km)

Sensitivity Analysis

Sensitivity analysis is a technique used to evaluate how changes in important process parameters of a model affect the variability of its output while keeping other variables constant. This study utilizes sensitivity analysis to estimate the effects of various TEA and LCA parameters typically evaluated in literature ^{23,33} on the NPV and the 100-year GWP of the six scenarios. For economic feasibility, the study varied the capital costs, internal rate of return, feedstock cost, catalyst cost, facility capacity, and product price by $\pm 20\%$ of base values. For the environmental impacts, the study varied the distance between the HDPE recovery facility to the refinery, natural gas, electricity, and diesel requirements of the refinery by $\pm 20\%$ of base values.

Results and Discussion

Techno-Economic Analysis

Figure S5 in SI shows the six scenarios' annual output broken down into ethylene, propylene, naphtha, diesel, and wax. Due to low residence time, the CPY and TOD scenario has significant wax in its product distribution. HRT scenarios have more naphtha and diesel in their product distribution because of the longer residence time in the pyrolysis unit; pyrolysis products get more time to break down into shorter chained hydrocarbons. In Scenarios with hydrocracking (CPY-HC, TOD-HC, HRT-HC), the long-chain hydrocarbons (wax) are broken down to diesel and naphtha, thereby increasing the amount of naphtha and diesel in their product distribution.

Figure 3A shows the Equipment cost breakdowns for all six scenarios. The fixed capital investment (FCI) ranges from \$32.4 million to \$244.0 million. For scenarios without product upgrading, TOD showed the lowest equipment cost because of the process intensification advantage of TOD over CPY discussed in Polin et al. ¹¹, which implies that for the same feed rate, TOD can utilize a smaller reactor compared to the reactor needed by conventional pyrolysis. Also, TOD equipment cost does not include the cost of an additional combustor unit that produces process heat for conventional pyrolysis. Scenarios with hydrocracking show higher capital costs because of the high cost of hydrocracking units. TOD and CPY, with hydrocracking, have significantly larger fixed capital costs because the product distribution contains a larger amount of wax in the pyrolysis products that require hydrocracking. Figure 3B shows the operating cost of the six scenarios. The annual operating cost of the six scenarios without depreciation ranged from \$7.6 to \$27.4 million. CPY without product upgrading resulted in the lowest operating cost, while TOD-HC had the largest annual operating cost due to the cost of electricity associated with product fractionation and hydrogen required for hydrocracking.

The annual revenue (Figure S6 in SI) for the six scenarios ranges from \$28.1 million to \$71.5 million. The annual revenue is dependent on the annual yields and the product distribution. For

scenarios with hydrocracking where wax is hydrocracked to more valuable products, annual revenue is larger than in scenarios where wax accounts for a significant percentage of the product yield. TOD-HC resulted in the largest annual revenue of \$71.5 million. High residence time conventional pyrolysis scenarios also have high annual revenue because its product distribution contains less wax and more valuable products. Figure 3C shows the six scenarios' net present value (NPV) for a facility lifetime of 20 years and 30 years. Plastic pyrolysis is a relatively new technology; hence, it makes sense to use a 20-year facility lifetime, but the study wanted to investigate the impact of a longer lifetime on the economic feasibility of the facility. For a 20-year facility lifetime, HRT has the most favorable NPV among all scenarios, while CPY-HC has the least NPV. Scenarios with hydrocracking have lower NPVs compared to the same scenario without hydrocracking. This showed that the added revenue from hydrocracking does not offset the added equipment cost needed to set up the facility. If the facility lifetime is increased from 20 years to 30 years, The NPV of the six scenarios improves and ranges from \$23.8 million to \$298.1million. The NPV reported for HRT is around a reasonable estimate of the NPV (\$367 and \$383 million for 500 tonnes per day facility) reported in Gracida Alvarez et al.¹⁷, given the difference in facility capacity.

The minimum selling price (MSP) of the primary products Figure 4 of each scenario was estimated using the discounted cash flow rate of return. The product with the largest fraction in the facility output is selected as the primary product of each scenario. Wax was selected as the primary product of CPY and TOD, while Naphtha was selected as the primary product of the other four scenarios. For CPY and TOD, the MSP for wax is \$0.13 and \$0.11 per kg, respectively. This is significantly smaller than the market price (\$1.989 per kg³⁴) of paraffin wax. However, it is important to note that the quality of the pyrolysis wax produced in these scenarios is not of the same quality as paraffin wax. The MSP of Naphtha for the other four scenarios ranges from \$0.53 to \$0.61 per kg. This range is smaller than the market price of \$0.86 per kg recorded by Gracida-Alvarez et al.¹⁷. However, the MSP for naphtha recorded in this study is greater than the five-year average of \$0.50/kg recorded by Yadav et al.¹³.

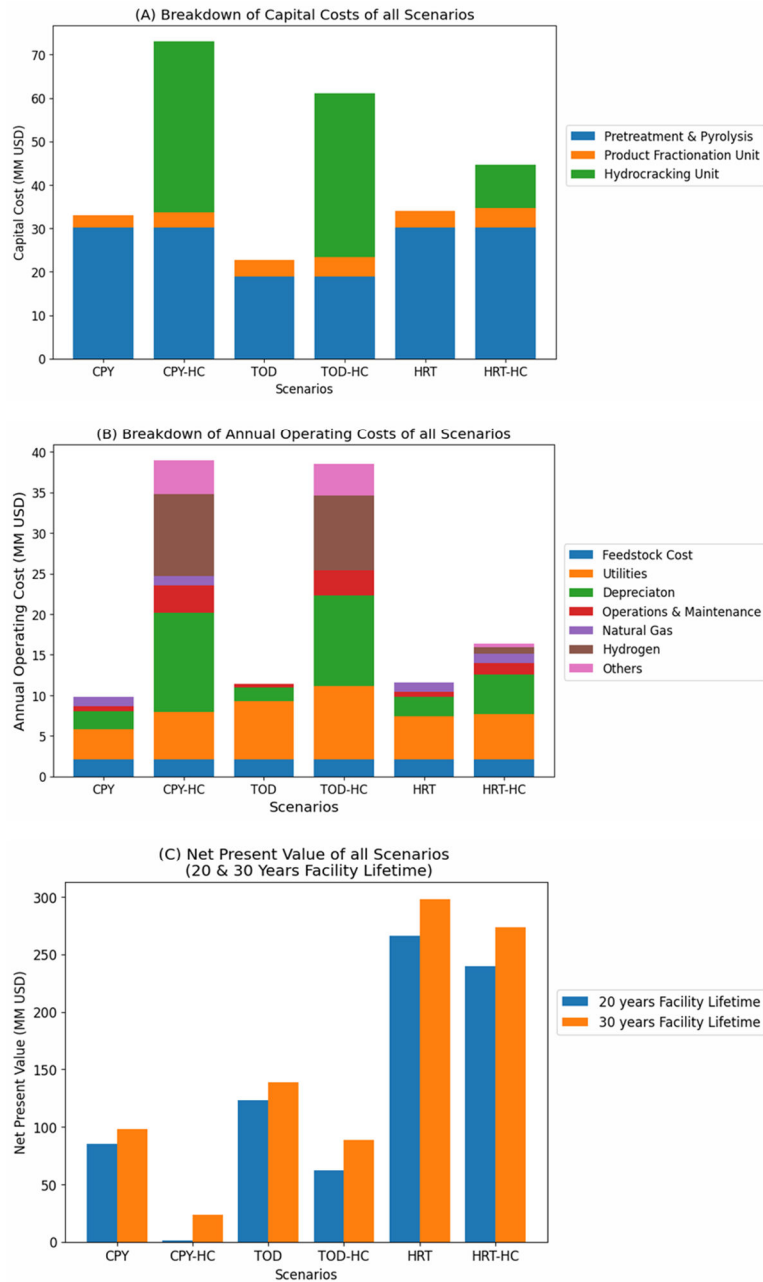


Figure 3. (A) Capital Cost breakdown of the six scenarios. (B) Operating Cost breakdown of the six scenarios. In the legend, Hydrogen represents the hydrogen used in hydrocracking, Natural gas for firing the combustors in conventional pyrolysis, others include catalyst cost and other process inputs. (C) The Net Present Value for the six scenarios at 20 and 30 years facility lifetime. labels for the six scenarios - (CPY: conventional pyrolysis without hydrocracking, CPY-HC: conventional pyrolysis with hydrocracking, TOD: Thermal oxo-degradation without hydrocracking, TOD-HC: Thermal oxo-degradation with hydrocracking, HRT: high residence time conventional pyrolysis with hydrocracking, HRT-HC: high residence time conventional pyrolysis with hydrocracking)

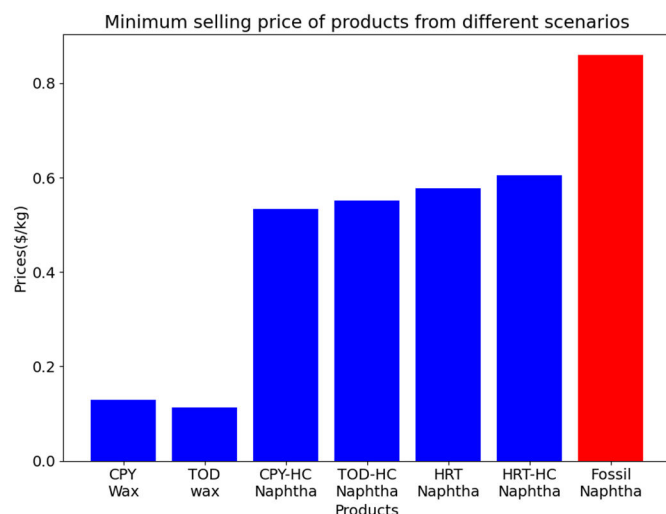


Figure 4. Minimum selling price of the primary products of the six scenarios and market price of Naphtha. CPY, CPY-HC, TOD, TOD-HC, HRT, and HRT-HC. (CPY: conventional pyrolysis without hydrocracking, CPY-HC: conventional pyrolysis with hydrocracking, TOD: Thermal oxo-degradation without hydrocracking, TOD-HC: Thermal oxo-degradation with hydrocracking, HRT: high residence time conventional pyrolysis with hydrocracking, HRT-HC: high residence time conventional pyrolysis with hydrocracking)

Life Cycle Assessment

The LCA results are shown in Figure 5. The 100-year GWP ranges from 314 to 1016 kg CO₂-eq per tonne of waste HDPE (Figure 5A). Scenarios without product upgrading have lesser 100-year GWP than scenarios with hydrocracking. For all scenarios, feedstock collection contributes 84.5 kg CO₂-eq per tonne of waste HDPE processed. This represents about 28% of the total 100-year GWP of scenarios without hydrocracking. TOD has a lesser 100-year GWP than CPY and HRT because it requires less natural gas for its operations. Scenarios with hydrocracking have a much higher 100-year GWP because of the added operations and hydrogen required for hydrocracking heavy hydrocarbons. Hence, unlike scenarios without hydrocracking, feedstock collection accounts for less than 10 % of the total emissions. For HRT-HC, the emissions were less than CPY-HC and TOD-HC because of the considerably lesser amount of longer-chain hydrocarbons that required hydrocracking.

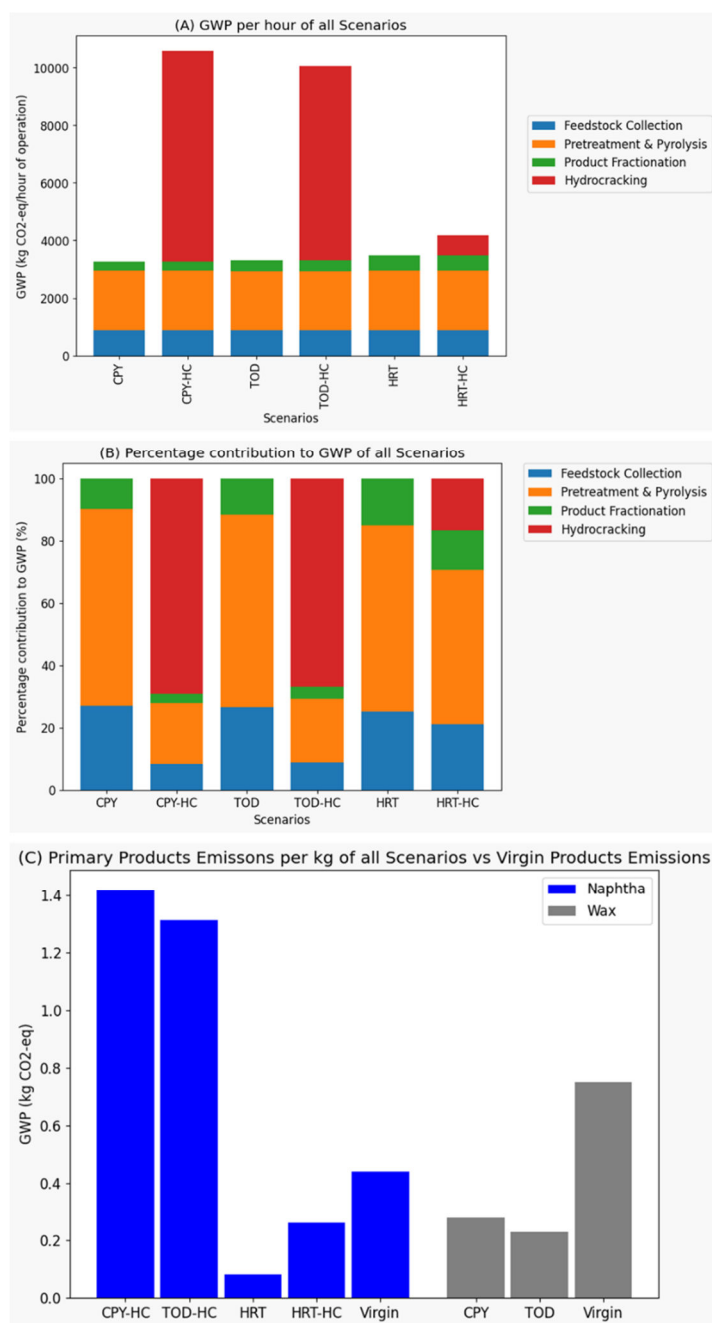


Figure 5. LCA results for the six scenarios CPY, CPY-HC, TOD, TOD-HC, HRT, and HRT-HC. (CPY: conventional pyrolysis without hydrocracking, CPY-HC: conventional pyrolysis with hydrocracking, TOD: Thermal oxo-degradation without hydrocracking, TOD-HC: Thermal oxo-degradation with hydrocracking, HRT: high residence time conventional pyrolysis with hydrocracking, HRT-HC: high residence time conventional pyrolysis with hydrocracking, GWP: Global warming potential)

To estimate the emissions associated with the primary products of each scenario, we assume that the co-products substitute the same product from a petrol-based process hereby generating credits for the scenarios. Figure 5C shows the emissions associated with producing the primary products from the six scenarios. For CPY and TOD, the emissions associated with wax produced are significantly lesser

than the emissions from virgin wax from fossil sources. CPY and TOD waxes might require more upgrading processes to attain the same quality as virgin wax. Hence, the emissions might increase. The emission associated with CPY-HC naphtha is 3 times more than the emissions of producing naphtha from the petroleum process, while TOD-HC naphtha is about 2.5 times the emissions of petroleum process naphtha. This significant increase is due to the high electricity and hydrogen requirements for hydrocracking heavy hydrocarbons to naphtha and diesel. HRT and HRT-HC naphtha resulted in negative emissions because the credits obtained from the co-products exceeded the emissions associated with the scenarios. As explained earlier, HRT and HRT-HC have lower emissions than other scenarios that produce naphtha as primary products because of the lesser electricity and hydrogen required for their operations.

Sensitivity Analysis

The sensitivity analysis was conducted on various facility parameters to assess the system's economic feasibility and environmental impact sensitivity to changes in various key parameters. Figure 6 summarizes the magnitude of the impacts of key parameters on the NPV. Wax prices, facility capacity, and internal rate of return significantly impact the NPV of TOD and CPY. A 20% increase or decrease in wax price can increase or decrease the NPV of CPY and TOD by 27% and 14%, respectively. A 20% change in facility capacity can also change the NPV of CPY and TOD by over 20%. FCI, facility capacity, and prices of primary products and diesel significantly impact the NPV of scenarios with hydrocracking. A 20% increase in FCI, a 20% decrease in Naphtha, or a 20% decrease in diesel price can cause conventional pyrolysis with hydrocracking to result in negative NPV. Ultimately, the sensitivity analysis showed that facility capacity, internal rate of return, FCI, and product prices are key drivers of the process economics.

The LCA sensitivity analysis results (Figure 7) showed that electricity consumption is a key driver of the 100-year GWP of all scenarios without hydrocracking. A 20% increase/decrease in the electricity requirement of the facility can result in a 15% increase or decrease in the 100-year GWP of scenarios without hydrocracking. For scenarios with hydrocracking, diesel for the hydrocracking unit and electricity are the key drivers of the environmental impacts. A 20% increase or decrease in diesel usage or electricity can increase or decrease the 100-year GWP by 10% for conventional pyrolysis and thermal oxo-degradation with hydrocracking. However, for high residence time conventional pyrolysis with hydrocracking, electricity is the key driver of emissions, with a 20% change in electricity requirement resulting in a 13% change in GWP, while a 20% change in diesel only changes the GWP by 3%. This shows that using electricity generated from renewable sources can significantly reduce the GWP of all scenarios.

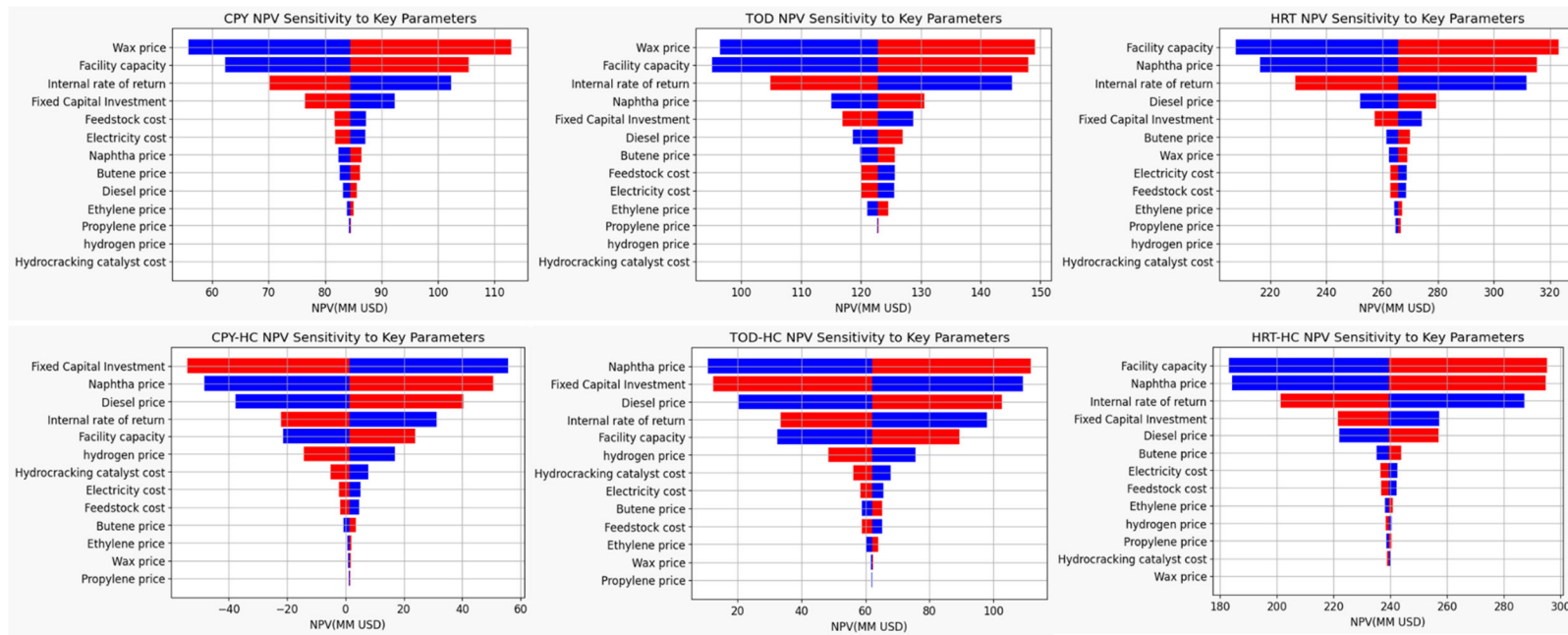


Figure 6. Sensitivity Analysis of key process parameters on the net present value for the six scenarios. CPY, CPY-HC, TOD, TOD-HC, HRT, and HRT-HC. (CPY: conventional pyrolysis without hydrocracking, CPY-HC: conventional pyrolysis with hydrocracking, TOD: Thermal oxo-degradation without hydrocracking, TOD-HC: Thermal oxo-degradation with hydrocracking, HRT: high residence time conventional pyrolysis with hydrocracking, HRT-HC: high residence time conventional pyrolysis with hydrocracking). Red bars show the NPV value for the lower case and blue bars show the NPV value for the upper case.

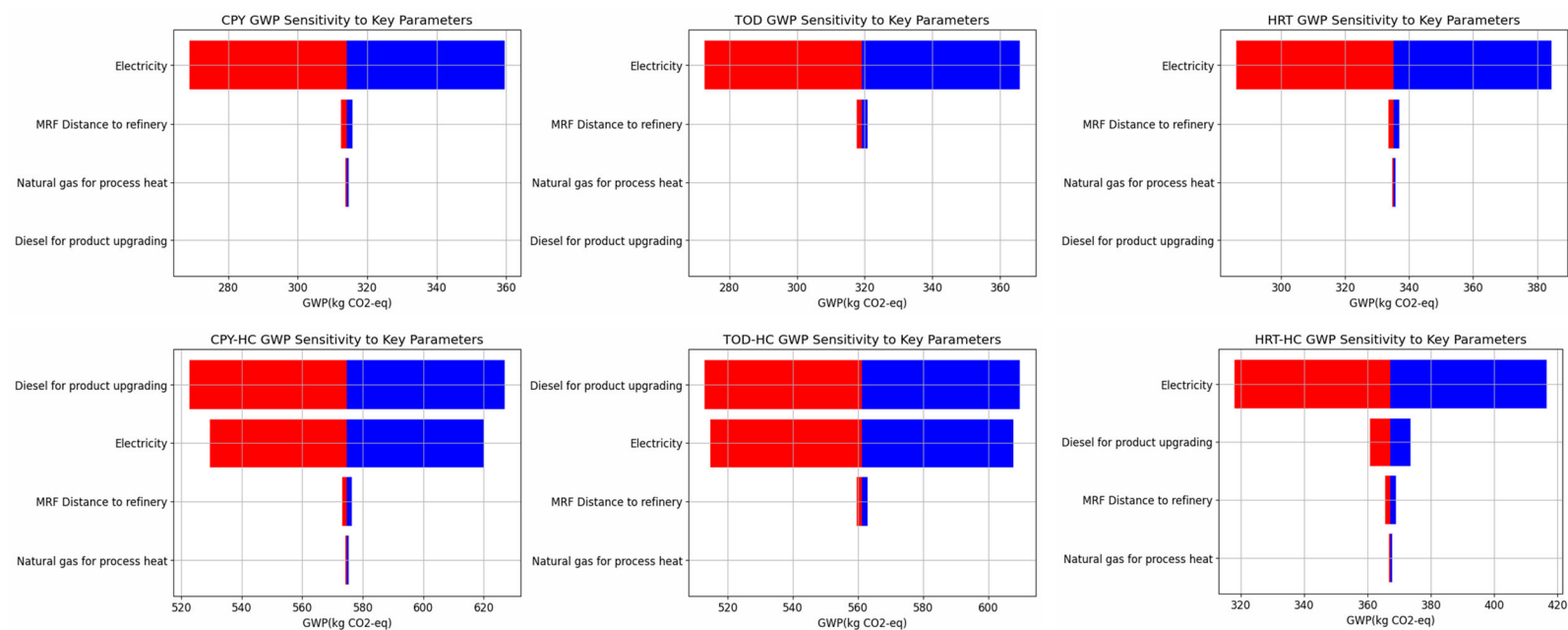


Figure 7. Sensitivity Analysis of key process parameters on the 100-year global warming potential of the six scenarios CPY, CPY-HC, TOD, TOD-HC, HRT, and HRT-HC. (CPY: conventional pyrolysis without hydrocracking, CPY-HC: conventional pyrolysis with hydrocracking, TOD: Thermal oxo-degradation without hydrocracking, TOD-HC: Thermal oxo-degradation with hydrocracking, HRT: high residence time conventional pyrolysis with hydrocracking, HRT-HC: high residence time conventional pyrolysis with hydrocracking). Red bars show the GWP value for the lower case and blue bars show the GWP value for the upper case.

Conclusion

The process economics and GWP for producing value-added products from the chemical upcycling of HDPE waste through conventional pyrolysis and thermal oxo-degradation with and without hydrocracking were investigated under six scenarios. The study found that high residence time conventional pyrolysis is the most economically favorable scenario, with a net present value of \$265.8 million over 20 years of facility lifetime. Although hydrocracking longer-chain hydrocarbons to more valuable naphtha and diesel can considerably increase annual revenue, the study found that it does not offset the high investment cost of adding the hydrocracking unit.

The study also found that the 100-year GWP can range from 314 to 1016 kg CO₂ -eq per tonne of waste HDPE processed in the facility. Thermal oxo-degradation and conventional pyrolysis without product upgrading are the most environmentally friendly scenarios among the six scenarios, with a total 100-year GWP of 319 and 314 kg CO₂ -eq per tonne of waste HDPE processed, respectively. Conventional pyrolysis with product upgrading is the least environmentally friendly, with a total 100-year GWP of 1016 kg CO₂ -eq per tonne of waste HDPE processed. Hydrocracking contributes more than 60% to the total emissions of the scenarios with hydrocracking because it is an energy-intensive process and requires hydrogen for its process.

Sensitivity analysis showed that product prices, facility capacity, capital investment, and internal rate of return significantly impact the net present value, while electricity, diesel, and distance of MRF facility are the biggest drivers of the 100-year global warming potential of the scenarios.

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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Supporting Information

The supporting information attached to this study contains more information on the techno-economic analysis and life cycle assessment. The process model codes and reports are available on GitHub via this link <https://github.com/lumedee007/TOD-CPY-TEA-LCA>

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