### Assessing the Technical Routes for Chemical Cycling of Waste Plastics to Light Olefins

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**ABSTRACT:** Waste plastics have become the second biggest environmental concern following climate change. The method for chemical cycling of waste plastics into light olefins is proposed. Four potential technical routes, that is, plastics to light olefins via syngas through the Fischer–Tropsch process (PFTO), plastics to light olefins via syngas through the recently developed OX-ZEO process (PZTO), plastics to light olefins via methanol through the methanol-to-olefins process (PMTO), and plastics to light olefins via pyrolysis oil and gas through hydrocracking and steam cracking process (PPTO), were studied. The carbon footprint, energy efficiency, and economic performance were analyzed based on techno-economic evaluation and life cycle assessment. The results demonstrated that the overall carbon efficiency of the PFTO, PZTO, PMTO, and PPTO routes was about 26.61, 67.59, 95.49, and 47.81%, respectively. The PMTO route had the highest carbon efficiency of the four routes. The energy efficiency and CO<sub>2</sub> emissions of PMTO were 55.60% and 0.55 t CO<sub>2</sub>/t olefin, respectively, better than the rest three routes with PFTO of 29.35% and 3.48 t CO<sub>2</sub>/t olefin, PZTO of 47.55% and 1.21 t CO<sub>2</sub>/t olefin, and PPTO of 47.21% and



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 $0.69 \text{ t CO}_2/\text{t}$  olefin. Production costs decreased as the carbon efficiency increased. The product costs of the PFTO, PZTO, PMTO, and PPTO routes were about 6003.36, 5400.23, 4918.59, and 6763.13 Chinese Yuan (CNY)/t olefin, respectively, which were calculated according to the price system of raw materials and products. In summary, PMTO is the most promising route with superior performance in CO<sub>2</sub> emissions, energy efficiency, and economics. As methanol-to-olefins (MTO) have already been commercialized, PMTO might provide a potential approach for large-scale cycling of waste plastics in the near future.

**KEYWORDS:** waste plastics, chemical cycling, light olefins, techno-economics, carbon footprint

#### 1. INTRODUCTION

Plastics play an important role in human daily life and are widely used in various fields of modern society such as architecture, healthcare, electronics, and automotive packaging.<sup>1</sup> With the rapid growth of the global population, the demand for plastic goods is increasing. In 2020, the global plastic production was approximately 367 million tons, which is expected to reach 1.1 billion tons by 2050.<sup>2</sup> However, plastics have caused a major environmental problem that humanity is facing because of poor waste management methods and inefficient recycling technologies, coupled with their extremely high durability. There were more than 350 million tons of plastic waste in 2018, of which less than 10% was recycled.<sup>3,4</sup> Waste plastic pollution has become the second biggest environmental concern in the world following climate change, which presents a great challenge to global sustainable development.

Many research projects have been conducted regarding the potential recycling/upcycling methods of waste plastics,<sup>5</sup> with the main products being fuels, naphtha, syngas, carbon dioxide, and light olefins. The methods of disposal of waste plastics can be summarized as linear and circular from the plastic life cycle

analysis.<sup>6</sup> The circular pathway of waste plastics mainly includes mechanical and chemical recycling compared to linear waste disposal, such as incineration and landfill. Unfortunately, disordered incineration can readily lead to serious air pollution while landfills could not only occupy large land area but also cause groundwater pollution. The methods of linear waste disposal are not eco-friendly and could result in continuous consumption of fossil resources. As a consequence of rapidly increasing cost and decreasing space for landfills, finding alternative options for waste plastics disposal is highly desired. Mechanical recycling has the advantage of low energy consumption and low costs.<sup>7</sup> However, mechanical recycling requires feedstocks exclusive of contamination and odorous constituents. In addition, one of the biggest shortcomings of mechanical recycling is that the recycled times would decrease

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Figure 1. Four routes for converting waste plastics to light olefins by chemical cycling.

because their inherent properties (strength and visual appeal) are degraded.  $^{8,9}$ 

Chemical recycling disposal of waste plastics plays a crucial role in the circular economy and enables closed loop recycling.<sup>10</sup> The most important benefit of chemical recycling is the capability to handle mixed plastic wastes (MPW) and create virgin-grade polymers for food packaging  $^{11}$  – a process called chemical upcycling. Dai et al.<sup>12</sup> adopted chemical methods to convert waste plastics into naphtha using catalytic pyrolysis technology. Park et al.<sup>13</sup> obtained product gases and pyrolysis oil by pyrolysis of polypropylene (PP) waste using the fluidized bed reactor. Gringolts et al.<sup>14</sup> reported converting plastic wastes into fuels and petrochemical. Pyrolysis products are mainly liquid, gas, and a bit of coke. Kaminsky et al.<sup>15,16</sup> discovered high-value chemicals, such as benzene, toluene, and xylene, in the pyrolysis. Among these valuable chemicals, xylene is an important component of gasoline.<sup>17</sup> In fact, converting plastic wastes into fuel oils<sup>18</sup> such as gasoline and diesel is not a real closed loop because the fuel oil will be burned out to release carbon dioxide, ending the cycle of matter and energy without considering the reuse of carbon dioxide as a feedstock to synthesize chemicals.<sup>19</sup> There is certainly beneficial potential with thermochemical processes. However, other chemical recycling technologies may also be of importance in the future, such as dissolution/purification and depolymerization technologies such as hydrolysis and solvolysis.<sup>20</sup> However, the technologies of dissolution and depolymerization of waste plastics face great challenges of solvent recovery and secondary pollution, and more environmental problems need to be solved in the process of industrialization.

The conversion of waste plastics to light olefins, although still in its infancy, shows great potential as an upcycling approach. Dong et al.<sup>21</sup> converted the plastic pyrolysis oil over ZSM-5 in a fixed bed reactor under 500 °C and 1 atm. They found that at a short contact time, the short-chain olefins are the main products while at a long contact time, the aromatics, paraffin, H<sub>2</sub>, coke, and methane are produced. Akin et al.<sup>22</sup> investigated different solid acid catalysts (HZSM-5, HZSM-22, SAPO-11, SAPO-34, and Al-MCM-41) for converting plastic waste to monomers by varying the vapor-catalyst contact time to maximize the light olefin recovery at 600 °C. They found that HZSM-5 demonstrates the highest activity and selectivity for light olefins, achieving a maximum  $C_2-C_4$  yield of 83.2 wt % with a 4 ms contact time. Eschenbacher et al.<sup>23</sup> obtained a light olefin yield of 69 wt % (19% ethylene, 22% propylene, 10% 1,3-butadiene, and 18% other C<sub>4</sub> olefins) by converting LDPE at 700 °C over the ZSM-5 catalyst. Onwudili et al.<sup>1</sup> found that catalysts would cause a reduction in oil yields and an increase in gas yields particularly at temperatures over 600 °C in the pyrolysis-catalysis of mixed plastics. Park et al.<sup>24</sup> pyrolyzed waste PE in a continuous two-stage pyrolysis process using an auger reactor and fluidized bed reactor. They found that as the temperature of the auger reactor elevated from 653 to 736 °C, the gas yield would significantly increase from 64 to 73 wt %. Simon et al.<sup>25</sup> used steam as a fluidization medium to pyrolyze mixed waste plastics at about 700 °C and obtained light olefins. The influence of feedstock flow rate, reactor type, and temperature on the pyrolysis of polyolefin was investigated by Westerhout et al.<sup>26</sup> They discovered that the temperature was the most sensitive factor. Microwave technology was employed for pyrolysis of heavier hydrocarbon liquids, and higher olefin yield was obtained on a pilot scale,<sup>27</sup> but it is an immense challenge to employ microwave pyrolysis to duel with a mass of waste plastics on the commercial scale, and

unaffordable energy consumption is also a restrained condition.

Although these experimental studies demonstrated the feasibility of chemical recycling processes converting waste plastics into light olefins on a laboratory scale, the systematic analysis of waste plastics to light olefins via process simulations is of practical significance from the viewpoint of circular economy. This is because, on the one hand, the emerging technologies have not been fully commercialized and, on the other hand, there is a lack of necessary process simulation data (energy demand, emissions). It is very important to explore the process operation parameters of four different routes and establish technical, economic, and environmental indicators for the industrial application and popularization of technology. These data indicators determined equipment selection, plant construction, technical route selection, and technical training. Therefore, establishing a database is very important and necessary based on calculating the material and energy balance and optimizing operating parameters before large-scale production. Therefore, we propose four technological routes of using the chemical cycle of waste plastics and enabling the reuse of these wastes back into virgin plastic. Four routes concerning the cycling of waste plastics into light olefins were considered in this work, as shown in Figure 1. In the first route, the waste plastics were directly cracked into syngas using a gasification process, and light olefins were produced from syngas through Fischer-Tropsch synthesis process, which is called PFTO. Jiao et al.<sup>28</sup> developed an oxide-zeolite (OX-ZEO) catalyst to synthesize light olefins from syngas with 83% light olefins selectivity (OS) and 85% CO conversion. The second route was similar to the first, but instead of Fischer-Tropsch synthesis, it used an oxide-zeolite (OX-ZEO) catalyst to convert syngas into light olefins named the PZTO route. The third route was called PMTO, in that light olefins were produced from syngas via methanol synthesis (MS) and a methanol-to-olefins (MTO) process. The fourth route is called PPTO. In this route, the pyrogas and oil were produced by pyrolysis of the mixed plastic waste (MPW) which consisted of polyethylene (PE), PP, and polystyrene (PS), and the main components of pyrogas were H<sub>2</sub>, CH<sub>4</sub>, and light olefins, which were separated by a distillation column. The pyrolysis oil was decomposed into light olefins by a hydrocracking and steamcracking process.

The main purpose of this work, therefore, was to assess the feasibility of these four routes based on the recently published experimental results together with some commercially available data. In doing so, process simulations of four routes were first conducted using the software Aspen Plus V11, where the impact of process conditions, such as the temperature, pressure, and steam/plastic ratio, were analyzed. Then, the feasibility study was performed from the perspective of  $CO_2$  emissions, energy efficiency, and economics to highlight the potential of these routes.

#### 2. MATERIALS AND MODELS

**2.1. Feedstock.** Polyolefins account for about 57% of the whole plastic market.<sup>29,30</sup> Reported in the literature,<sup>31</sup> waste packaging materials containing the above-mentioned polymers account for about 70% of the total plastic waste, and the main component of the wastes is PE.<sup>32</sup> Table 1 presents the composition of the plastics in municipal solid waste in China.<sup>33–36</sup> As shown in Table 1, PE is dominant, followed by PP. In this work, the MPW was assumed composed of 60% PE, 28% PP, and 12% PS as the feedstock, approximating the recycling plastic waste in China.

 Table 1. Proportion and Sorts of Recycling Plastic Waste in

 China<sup>34</sup>

type of material	China (wt %) <sup>34</sup>	Simulated (wt %)
PE	45	60
PP	28	28
PS	17	12
PET	4	
others	6	

The waste plastics were pretreated before they entered the gasifier for cracking. The pretreating process included washing, drying, and crushing; and the obtained fragments have an average particle size ranging from 2 mm to 5 mm. Table 2 provides an overview of the key characteristic parameters of PE, PP, and PS, which are then used to derive the corresponding parameter of MPW based on their respective weights.

Table 2. Main Characteristics of MPW

items	PE <sup>37</sup>	PP <sup>37</sup>	PS <sup>35</sup>	MPW
moisture Content (wt %)	0.02	0	0.3	0.05
proximate analysis, wt %				
fixed carbon	0	0	1.30	0.16
volatile matter	99.85	99.30	94.20	99.02
ash	0.15	0.70	4.50	0.83
ultimate analysis, wt %				
carbon	85.81	86.42	84.48	85.82
hydrogen	13.86	12.28	8.86	12.82
oxygen	0	0		0.00
nitrogen	0.12	0.72	0.09	0.28
sulfur	0.06	0.17	0.01	0.08

The analysis revealed that PE, PP, PS, and MPW exhibit a minimal moisture content ranging from 0 to 0.3%. They have significant volatile matter contents, ranging from 94.20 to 99.85%. The ash content is relatively low, varying from 0.15 to 4.50%, while the fixed carbon content remains low, between 0 and 1.3%. The presence of high volatile matter could contribute to an increase in the liquid products.<sup>38,39</sup> The simulation results indicate that the quantity of nitrogen (N) and sulfur (S) could be negligible.<sup>40</sup>

2.2. Process Simulation. The software of ASPEN Plus V11 was used to simulate material and energy balances in four routes.<sup>41</sup> The disposal capacity of waste plastics was set to  $30 \times 10^4$  t/y, and the run-time per year was 8000 h. Sahu et al.<sup>18</sup> discussed three treatment scales for converting waste plastics into fuel oil in 2014, and the economic analyses for small, medium, and large scale have been done. In these three cases, the amount of waste plastics treated in the medium scale was 60,000 tons/y, and the larger scale was 120,000 tons/y. With the continuous development and progress of technology, combined with the treatment scale of coal to olefins,<sup>42</sup> we believed that the amount of waste plastics in a single set of equipment set to 300,000 tons/year was more reasonable. According to the China Materials Recycling Association, 62 million tons of plastic waste was produced and 19 million tons was recyclable plastic waste in China in 2021.<sup>43,44</sup> The single-unit processing capacity we assumed was about 0.48% of the annual output of waste plastics, which is about 1.6% of recyclable plastic waste in China. In the waste plastics to olefins (PTO) simulations, each route was divided into several unit operations. The specific operating conditions are described in the following sections.

**2.3. PFTO and PZTO Routes.** The PFTO route comprises two stages, namely, gasification and syngas to olefins (STO), as shown in Figure 2. It is assumed that MPW was fed to the gasification pyrolysis reactor operating under pressure of 1 atm and temperature of 900  $^{\circ}$ C.<sup>18</sup> The syngas was obtained at a steam/plastics (S/P) ratio of 1.25.<sup>18,25</sup> Unlike the crude syngas from coal gasification, the syngas

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Figure 2. Simple block diagram of PFTO and PZTO routes flow.



Figure 3. Simulation process flow diagram of PFTO/PZTO.





obtained from waste plastics was much cleaner than that from coal gasification (CG). According to the elemental analysis of waste plastics shown in Table 2, it can be seen that the elemental composition of waste plastics is mainly carbon and hydrogen, while coal also contains N, S, O, Al, Si, Fe, and other elements. In comparison, the elemental composition of coal is more complex, and there are more impurities than waste plastics in the product. Therefore, the operation units of water–gas shift (WGS) and acid gas removal (AGR) could be ignored here, which, however, should be considered in the coal-to-olefins (CTO) process. The light olefins are obtained from the unit operation of FTO. The simulation process flow diagram is shown in Figure 3.

In the PFTO or PZTO route, waste plastic is first converted into syngas by gasification unit operation.<sup>37</sup> After being pressurized and preheated, the syngas enters the olefin synthesis reactor. Two different processes are simulated in the olefin synthesis unit operation.<sup>45,46</sup> One is the Fischer–Tropsch synthesis process to olefins (FTO),<sup>47</sup> and the other is the syngas through the oxide-zeolite one-step process for olefins (ZTO).<sup>28</sup> The final step is the separation and purification of olefins, which we call the distillation unit operation shown in Figure 3.

**2.4. Gasification Unit.** The MPW, which are nonconventional components, will be first decomposed into elements and then sent to reaction in the simulations. Therefore, the gasification unit is divided into two parts: decomposition and reaction, as shown in Figure 4.

RStoic and RGibbs reactor models were used in the decomposition unit and gasifier unit,<sup>37</sup> respectively.

The steam gasification reactions are as follows.

~ ~

$$C + CO_2 \rightarrow 2CO \quad \Delta H_{298.15K} = 172 \text{kJ/mol}$$
(1)

$$C + H_2O \rightarrow CO + H_2 \quad \Delta H_{298.15K} = 131 \text{kJ/mol}$$
 (2)

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad \Delta H_{298,15K} = 206 \text{kJ/mol}$$
 (3)

2.5. Syngas to Olefins Unit. Much more attention has been paid to the Fischer-Tropsch synthesis recently because FTO presents a shorter conversion route. However, the FTO products are complicated mixtures, and the selectivity of olefins needs to be further improved. The main reactions are shown in Eqs. 4-8.45,46

$$nCO + 2nH_2 \rightarrow 2C_2H_{2n} + nH_2O \tag{4}$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O \tag{5}$$

$$nCO + (2n + 1)H_2 \rightarrow C_2H_{2n+2} + nH_2O$$
 (6)

$$nCO + 2nH_2 \rightarrow C_2H_{2n+2}OH + (n-1)H_2O$$
 (7)

$$\rm CO + H_2O \rightarrow \rm CO_2 + H_2 \tag{8}$$

Peron et al.<sup>47</sup> reported the 53% selectivity for hydrocarbons over iron catalysts in a conventional fixed bed reactor under the conditions of 1.0 MPa, 350 °C,  $H_2/CO = 1/1$ , and WHSV = 3.6 L/(g·h). He has made a series of iron-based catalysts with CO conversion in the range of 8-53% and hydrocarbon selectivity in the range of 51-85%, and Fe  $(20\%)/SiO_2$  has the highest light olefin selectivity, which is what we need, as shown in Table 3. Jiao et al.<sup>28</sup> developed an oxide-zeolite

#### Table 3. Conversion and Selectivity in the STO Unit

item	$FTO (OS = 34\%)^{47}$	ZTO $(OS = 83\%)^{28}$
CO conversion (%)	14	85
$CO_2$ selectivity (%)	47	41
hydrocarbon selectivity (%)	53	59
CH <sub>4</sub>	24	2
$C_2^{=}-C_4^{=}$	34	83
$C_2^{0} - C_4^{0}$	6	9
C <sub>5+</sub>	36	6
catalyst	Fe (20%)/SiO <sub>2</sub>	ZnCrO <sub>x</sub> -GeAPO-18 <sub>0.027</sub>

(OX-ZEO) catalyst to synthesize olefins from syngas with 56-84% CO conversion and 80-89% light olefins (two to four carbon atoms,  $C2^{=}-C4^{=}$ ) selectivity (OS). syngas reaction was carried out in a fixed bed reactor at the conditions of  $H_2/CO = 2.5$ , 430 °C, 6 MPa, 1.50  $L/(g\cdot h)$ , under which 85% of CO is converted, 83% OS, and 9% lightparaffins (two to four carbon atoms,  $C_2^{0}-C_4^{0}$ ) selectivity as shown in Table 3. In this work, the RYield model was selected to simulate FTO reactors and the ZTO process. The discrepant conversion and selectivity with different catalysts are shown in Table 3.28,4

These two approaches for syngas to olefin show great potential for commercialization. The simulation results of the PFTO route are presented in Table 4.

2.6. PMTO Route. The PMTO route comprises three units, namely, gasification, MS, and MTO, as shown in Figure 5. Unlike PFTO, syngas can be first used to synthesize methanol, and light olefins can be obtained from the unit operation of MTO in the PMTO route, as shown in Figure 6.

In the PMTO route, the Aspen model and operation parameters are shown in Table 5.

2.7. Methanol Synthesis Unit. Methanol is obtained in the MS reactor, and the major reactions are as follows.

$$CO + 2H_2 \rightarrow CH_3OH \quad \Delta H_{298.15K} = + 90.77 \text{kJ/mol}$$
(9)

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components

PE

PP

PS

H<sub>2</sub>

H<sub>2</sub>O

СО

CO<sub>2</sub>

CH₄

 $C_2H_4$ 

 $C_2H_6$ 

(4)	C <sub>3</sub> H <sub>6</sub>	0	0
(4)	C <sub>3</sub> H <sub>8</sub>	0	0
(5)	$C_4H_8$	0	0
	$C_4H_{10}$	0	0
(6)	C5H12	0	0
	total flow (kg/h)	84375	84375

pressure (MPa)

temperature (°C)

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \quad \Delta H_{298.15K} = + 49.16 \text{kJ/mol}$$
(10)

0.10

500

$$CO_2 + H_2 \rightarrow CO + H_2O \quad \Delta H_{298.15K} = + 41.21 \text{kJ/mol}$$
 (11)

The syngas after steam cracking from MPW and mixed unreacted gas from the flash drum was used as the raw material for methanol synthesis. Mixed with the circulating gas, syngas was pressurized to 5.0 MPa in the compressor C101 and then preheated to 240 °C by the preheater H101 before entering the synthesis reactor MS for reaction.<sup>49-51</sup> The gas from the synthesis reactor was cooled to 40 °C by the cooler H102 and then sent to the Flash Drum F101 for separating the unreacted syngas. The separated gas was divided by a splitter to circulate into the system. The crude methanol separated from the Flash Drum F101 was sent to the rectifying column. The rectifying column T001 was composed of 26 column plates. After one time of distillation of crude methanol, 99.6 wt % methanol can be obtained.<sup>51</sup> In the simulations, the RStoic model was used for reactor MS, the Flash model was used for Flash Drum, and the RadFrac model was used for the rectifying column.

2.8. Methanol-to-Olefins Unit. The MTO unit includes the MTO reaction, separation, and purification processes. The MTO unit was simulated based on DMTO technology that has been successfully industrialized.<sup>52-54</sup> The RYield model was used to simulate the synthesis of light olefins. The RadFrac model was used for the separation tower. The HeatX model was used to simulate the heat exchanger. The methanol conversion rate was set as 99.90% under a reaction of 500 °C and 0.22 MPa. The products obtained in final separation were 99.66% ethylene and 83.82% propylene in purity, respectively.52-54

2.9. PPTO Route. The PPTO route comprises three stages, namely, pyrolysis, power to hydrogen (PtH) and hydrofining, and steam cracking (SC) as shown in Figure 7.

Waste plastics (60% PE, 28% PP, and 12% PS) were fed to the pyrolysis reactor. Under the temperature of 500 °C and the pressure of 0.1 MPa, the pyrolysis gas and oil were produced with the catalyst.<sup>55</sup> Indeed, a higher temperature favors the production of pyrolysis gas. However, a higher temperature indicates much more energy consumption, which, in turn, implicitly increases the production costs. In addition, the compositions of pyrolysis gas obtained at a higher temperature would be much more complicated (including hydrogen, methane, ethane, etc.),<sup>23,24</sup> which reduces the yield of the target product (ethylene, propylene, and butene) and the carbon utilization efficiency. The product gas was generally less than 10%, and the pyrolysis oil was the main component. The alkenes and some aromatics in the pyrolysis oil can be converted into paraffin

Е

0

0

0

0

0

ZTO

31819.90

20846.90

218.71

3241.14

1545.95

5931.29

1120.81

16205.70 1477.34

1967.25

84375

4.00

420

FTO

0

0

0

0 28220.70

0

25266.60

2492.68

1370.72

734.65

2570.19

366.25

6182.12

355.05

16816

84375

1.00

350

0

0

0

syngas

10024.90

71348.80

549.73

542.08

1909.03

0.39

0.06

feedstock

22500

10500

4500

46875.00

0

0

0

0

0

0

0.10

25



Figure 5. Simple block diagram of PMTO.



Figure 6. Simulation process flow diagram of PMTO.

alkanes by the hydrocracking process at a temperature of 380 °C and pressure of 3 MPa.<sup>56,57</sup> Light olefins were obtained from hydrogenated pyrolysis oil using a steam cracking process at a temperature of 650 °C and pressure of 0.1 MPa.<sup>3</sup> The simulation process flow diagram is presented in Figure 8. In the hydrogenation unit, hydrogen is presumed to be derived from electrolysis of water using renewable energy, which can be wind power, solar PV, hydropower, and/or nuclear power.<sup>58,59</sup> In 2022, renewable energy generation reaches 2.7 trillion KWH, accounting for 31.6% of the total electricity consumption in China, with an increase of 1.7% over 2021. This is roughly equivalent to the reduction of carbon dioxide emission of about 2.26 billion tons.<sup>60</sup> In fact, renewable electricity has become much more available in China due to technological developments and policy guidance in recent years. Adding green hydrogen to the PPTO route can improve the carbon efficiency and contribute to environmental sustainability.

The direct catalytic cracking of pyrolysis vapors could be an alternative route within PPTO. However, we did not consider it in this work owing to the complex composition of pyrolysis vapors and low yield of light olefins<sup>17,22</sup> on the one hand and hydrogenation of tar and polycyclic aromatics to avoid rapid catalyst deactivation on the other hand. However, a more efficient yet realistic PPTO route, that is, pyrolysis + hydrotreating + steam cracking, has been considered.

**2.10. Pyrolysis Unit.** The MPW was decomposed into pyrolysis oil and pyrogas at a high temperature with or without catalyst. The general reaction is as follows.

Waste plasics  $\rightarrow$  pyrolysis oil + pyrogas (12)

The Aspen model and operating parameters are presented in Table 6.55

The pyrogas accounts for 5.34% of the total pyrolysis products, and pyrolysis oil accounts for 94.66%. The specific product distribution is illustrated in Table 7.

**2.11. Steam Cracking.** The hydrogenated pyrolysis oil was fed into the steam cracking reactor with a S/CH mass ratio of 0.35, at a temperature of 650 °C and pressure of 0.1 MPa.<sup>3,18,55</sup> The steam cracking product yields are shown in Table 7. It can be seen from Table 7 that there were a few unsaturated alkenes and aromatics in the pyrolysis oil. To obtain more olefins, hydrogenation was further carried out before steam cracking, and hydrogen is assumed to be green hydrogen from electrolysis of water using renewable energy.<sup>61,62</sup>

**2.12. Life Cycle Assessment and Techno-Economic Analysis.** Under the target of carbon neutrality, it is important and necessary to analyze the carbon footprint. The carbon footprints from raw materials to products were evaluated using the life cycle assessment methods.<sup>63</sup> Monitoring carbon emissions can assist in decision-making, concerning carbon emission reduction. The parameters for carbon footprint analysis are listed in Table 8.

The four basic steps of the life cycle assessment  $(LCA)^{67-69}$ include system boundary, inventory data, impact assessment, and interpretation. As mentioned above, four technical routes for converting waste plastics into light olefins were examined in this work. Therefore, the system boundary of LCA was from the MPW to the light olefins. Inventory databases are mainly derived from the literature and publicly available databases.<sup>70-73</sup> In this work, we focus on carbon dioxide emissions; hence, this is called Carbon Footprint Analysis under the environmental life cycle assessment. In addition,

Table 5. Design Assumptions Made for the PMTO Process Simulations  $^{\rm 48}$ 

equipment	equipment code	aspen model	assumption
DECOM	DECOM	RStoic	mixed plastics waste = $37,500$ kg/h, temperature = $500$ °C, $P = 1$ atm
gasifier	GASIFIER	RGibbs	temperature = 900 °C, $P = 1$ atm, steam/plastic= 1.25
methanol synthesis	MS	RStoic	temperature = 240 °C, $P = 50$ atm
flash separation tank	F101	Flash Drums	temperature = 40 °C, $P = 10$ atm
methanol distillation column	T001	RadFrac	column plate= 26, methanol = 99.6%
MTO reactor	МТО	RYield	temperature = 520 °C, $P = 2$ atm
flash separation tank	F102	Flash Drums	temperature = 10 °C; $P = 0.78$ atm
depropanizator	T101	RadFrac	column plate = 52, $P = 1.50$ atm
debutanizer	T102	RadFrac	column plate = 85, $P = 0.87$ atm
demethanizer	T201	RadFrac	column plate = 50, $P = 2.00$ atm
dethanizer	T202	RadFrac	column plate = 50, $P = 1.98$ atm
ethylene rectification tower	T301	RadFrac	column plate = 70, $P = 1.68$ atm
propylene rectification tower	T302	RadFrac	column plate = 70, P = 1.65 atm

the economic life cycle assessment (E-LCA) method is also involved in this study. In the carbon footprint analysis process, we applied the energy analysis module in ASPEN Plus V11 software to calculate the CO<sub>2</sub> emissions of each unit operation. The operation units of gasification, SC, MS, MTO, and STO, were modeled and described using Aspen Plus V11 in Section 2. For PFTO, PZTO, PMTO, and PPTO routes, the disposing capacities of waste plastics were set as the same, that is,  $30 \times 10^4$  t/y. Based on the simulation results, we can further calculate the energy efficiency, CO<sub>2</sub> emissions, and product cost.

Energy efficiency is determined by eq  $13^{74}$ :

$$\eta = \frac{E_{\text{olefins}}}{E_{\text{MPW}} + E_{\text{util}}} \tag{13}$$

where  $\eta$  is the energy efficiency of MPW to light olefins,  $E_{\text{olefins}}$  is the energy in light olefins,  $E_{\text{MPW}}$  is the energy in MPW, and  $E_{\text{util}}$  is the energy from utilities (including steam and electricity). Hydrogen comes from the electrolysis of water; therefore, the energy input for hydrogen comes from electricity, which is included in utilities. We calculated energy efficiency according to the lower heating values of MPW, ethylene, propylene, and butylene (27.30 MJ/kg, 59428.64, 87592.05, and 117593.11 kJ/Nm<sup>3</sup>, respectively).<sup>37</sup>

Product cost, which is one of the important parameters indicating the economic performance of the technical routes, includes the cost of raw material, utilities, operation and maintenance, depreciation, plant overhead, administrative, distribution, and selling cost. The equipment investments were estimated according to the literature data<sup>42,75</sup> as shown in Table 9. The equipment investment was calculated based on the treatment scale referred to the equipment investment of coal to olefins.<sup>75</sup> As can be seen from Table 9, different waste plastic treatment process routes require different equipment investments. The longer the process route, the more the equipment investment.

The costs were calculated based on the prices of raw materials and products, as shown in Table 10.<sup>76,77</sup> The product cost was calculated based on their ratios.<sup>42</sup> We assumed that the life span of the equipment was 30 years with a salvage value of 4%, and the straight-line method was used to calculate the depreciation cost.<sup>78</sup>

Coal is used as a raw material for traditional coal-to-olefins in Table 10, which is used as a reference for comparison with PTO routes.

#### 3. RESULTS AND DISCUSSION

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**3.1. Product Distribution.** The gasifier temperature, pressure, and S/P mass ratio are the main factors that influence the composition of syngas. The optimum simulation results were obtained at a temperature of 900 °C, pressure of 1 atm, and S/P of 1.25, and the molar composition of the simulation compared to the experimental results is presented in Table 11. As can be seen, the simulation results are closely aligned with the experimental results, <sup>79–81</sup> so the model can be used in MPW to syngas via gasification processes.

Figure 9 shows the effect of gasifier temperature on the composition of syngas from MPW. In this simulation, the reaction temperature was controlled from 700 to 1100 °C while S/P is fixed at 1.25. Increasing the temperature resulted in an increase of H<sub>2</sub> and CO while decreasing CO<sub>2</sub>, CH<sub>4</sub>, and



Figure 7. Simple block diagram of PPTO process flow.



Figure 8. Simulation process flowchart of PPTO.

# Table 6. Design Assumptions Made for the PPTO ProcessSimulations

equipment	equipment code	aspen model	assumption
DECOM	DECOM	RStoic	mixed plastics waste = $37,500$ kg/h, temperature = $500 \degree C$ , P = 1 atm
pyro	PYRO	RYield	temperature = 500 °C, $P = 1$ atm, ZN-CATALYST <sup>55</sup>
hydro	HYDRO	RYield	temperature = 380 °C, $P = 30$ atm <sup>56,57</sup>
steam	STEAM	RYield	temperature = $650 \text{ °C}$ , $P = 1$ atmS/CH = $0.35 \text{ 3}$
flash separation tank	F001	Flash Drums	temperature = 20 °C, $P = 0.78$ atm
flash separation tank	F102	Flash Drums	temperature = 40 °C, $P = 0.56$ atm
depropanizator	T101	RadFrac	column plate = $26$ , $P = 1.5$ atm
debutanizer	T102	RadFrac	column plate = 55, $P = 0.87$ atm
demethanizer	T201	RadFrac	column plate = $45$ , $P = 1$ atm
dethanizer	T202	RadFrac	column plate = 40, P = 1.25 atm
ethylene rectification tower	T301	RadFrac	column plate = 60, P = 1.26 atm
propylene rectification tower	T302	RadFrac	column plate = 40, $P = 1.35$ atm

 $\rm H_2O$ . An increase in temperature is conducive to endothermic reactions, and thus, the components of  $\rm H_2$  and CO are higher, while the fractions of  $\rm CH_4$ ,  $\rm CO_2$ , and  $\rm H_2O$  are lower. However, when the temperature exceeded about 900 °C,  $\rm H_2$  and CO would remain stable.

components	feedstock	pyrolysis product	hydro- cracking	steam cracking
PE	22,500	0	0	0
РР	10,500	0	0	0
PS	4500	0	0	0
H <sub>2</sub>	0	29.89	0	257.08
$H_2O$	0	0	0	5484.35
СО	0	0	0	3427.72
CO <sub>2</sub>	0	0	0	856.93
$CH_4$	0	771.98	0	2013.78
$C_2H_4$	0	760.16	0	10497.38
$C_2H_6$	0	38.78	0	5141.58
$C_3H_6$	0	281.51	0	5441.50
C <sub>3</sub> H <sub>8</sub>	0	119.89	0	7712.36
$C_4H_8$	0	0	0	2013.78
C <sub>4</sub> H <sub>10</sub>	0	0	0	0
C5H12	0	6170.93	11964.73	0
C <sub>6</sub> H <sub>14</sub>	0	14586.15	15308.76	0
C <sub>7</sub> H <sub>8</sub>	0	215.51	77.85	0
C <sub>7</sub> H <sub>14</sub>	0	5610.15	0	0
C <sub>7</sub> H <sub>16</sub>	0	0	6281.90	0
C <sub>8</sub> H <sub>8</sub>	0	6912.34	0	0
C8H18	0	1137.15	213.23	0
C <sub>9</sub> H <sub>8</sub>	0	37.13	0	0
C <sub>9</sub> H <sub>10</sub>	0	252.60	0	0
C <sub>9</sub> H <sub>12</sub>	0	561.08	0	0
$C_{10}H_{10}$	0	14.78	0	0
total flow (kg/h)	37500	37500	33846.47	42846.47
pressure (MPa)	0.1	0.1	3	0.1
(°C)	25	500	380	650

Table 7. Simulation Result of PPTO

#### Table 8. Parameters for Carbon Footprint Analysis<sup>64</sup>

item	mater	and energy	parameter	source
input	MPW		85.82%	31,33
output	hydroc	arbon	simulation result	
electricity				
consumption of 37,500 MPW	kg/h 477 G	ſ/h		
electricity emission fact	or 0.531 MW	t CO <sub>2</sub> /		65
steam	0.0341	2 kgce/MJ		66

#### Table 9. Equipment Investments in Four Routes<sup>75</sup>

items	PFTO	PZTO	РМТО	РРТО
gasification reactor (×10 <sup>4</sup> CNY)	39,000	39,000	39,000	48,000
methanol synthesis reactor (×10 <sup>4</sup> CNY)			14,800	
methanol distillation column (×10 <sup>4</sup> CNY)			16,600	
olefin synthesis reactor (×10 <sup>4</sup> CNY)	23,400	23,400	21,000	
water electrolyzer (×10 <sup>4</sup> CNY)				76,400
hydrogenation reactor (×10 <sup>4</sup> CNY)				45,800
steam cracking reactor (×10 <sup>4</sup> CNY)				32,000
depropanizator (×10 <sup>4</sup> CNY)	15,600	15,600	15,600	24,300
debutanizer (×10 <sup>4</sup> CNY)	16,500	16,500	16,500	18,700
demethanizer (×10 <sup>4</sup> CNY)	12,500	12,500	12,500	14,300
dethanizer (×10 <sup>4</sup> CNY)	17,800	17,800	17,800	19,600
ethylene rectification tower $(\times 10^4 \text{ CNY})$	15,600	15,600	15,600	20,300
propylene rectification tower (×10 <sup>4</sup> CNY)	15,600	15,600	15,600	18,600
total Equipment investment (×10 <sup>4</sup> CNY)	156,000	156,000	185,000	318,000

Table 10. Prices of Raw Materials and Products (CNY/ t)<sup>76,77</sup>

items	price	items	price	items	price	
MPW	400	steam	200	electricity <sup>a</sup>	0.65	
ethylene	8800	cooling water	3	$H_2$	10000	
propylene	7600	process water	15	butylene	9100	
<sup>a</sup> Unit of Electricity is kW●h.						

## Table 11. Comparison of Syngas Composition in the Gasification Unit

experimental result <sup>79</sup>	experimental result <sup>80</sup>	experimental result <sup>81</sup>	simulation value
0.777	0.683	0.640	0.646
0.113	0.261	0.257	0.333
0.019	0.039	0.064	0.002
0.049	0.013	0.033	0.012
0.042	0.004	0.006	0.007
	experimental result <sup>79</sup> 0.113 0.019 0.049 0.042	experimental result79experimental result800.7770.6830.1130.2610.0190.0390.0490.0130.0420.004	experimental resultexperimental resultexperimental result0.7770.6830.6400.1130.2610.2570.0190.0390.0640.0490.0130.0330.0420.0040.006

In this work, the pressure was controlled from 0.06 to 1.0 MPa while the temperature was fixed at 900 °C and the S/P was fixed at 1.25, as shown in Figure 10. A higher pressure would result in the reduction of H<sub>2</sub> and CO but an increase of CO<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub>O. This means that raising the reaction pressure favors the reduction in the volume of the products.



Figure 9. Effect of the temperature on the components of syngas.



Figure 10. Effect of the gasifier pressure on the distribution product.

The S/P mass ratio affects the composition of syngas. The composition of syngas is investigated as the S/P mass ratio increases from 0.25 to 2.5 at a temperature of 900 °C, as shown in Figure 11. Increasing S/P from 0.5 to 1.25 favors the production of hydrogen. The mole fraction of H<sub>2</sub> decreases when the S/P ratio exceeds 1.25. When the amount of steam increases to a maximum, a surplus of unreacted steam might be left. The remaining steam will react with CO and increases the percentage of CO<sub>2</sub> and H<sub>2</sub>, as shown in Equation 8. However, the increased rate of water vapor is greater than that of hydrogen in the composition of syngas, as shown in Figure 11. Therefore, an optimal S/P ratio of 1.25 would be expected because it provides the suitable components of syngas.

**3.2. Carbon Footprint.** Take a plant converting  $30 \times 10^4$  t/y MPW into light olefins for example, the carbon flow of life cycle assessment for four routes is shown in Figure 12.

37500 kg/h waste plastics (37,500 kg/h) were used as raw material, in which the carbon content was about 85.82%. In the PFTO and PZTO routes, around 99.92% carbon in MPW was converted into syngas in the steam cracking process; and 26.95



Figure 11. Effect of S/P on the distribution product.

and 67.64% carbon were, respectively, converted into light olefins. In the PMTO route, the gasification process is considered the same as that in the PFTO and PZTO routes. Following the MS and MTO units, 99.46% carbon in the syngas was converted to methanol, and 96.30% carbon in the methanol was converted into light olefins. In the PPTO route, the carbon efficiencies of pyrolysis, hydrocracking, and steam cracking were 94.59, 75.09, and 67.32%, respectively. Therefore, the overall carbon efficiencies of PFTO, PZTO, PMTO, and PPTO routes were about 26.61, 67.59, 95.49, and 47.81%, respectively. The PMTO route has the highest carbon efficiency of the four routes. For the PFTO route, decreasing CO<sub>2</sub> selectivity and improving olefins selectivity by using highly efficient catalysts could dramatically increase the yield of light olefins. For the PPTO route, longer process chains and widespread products result in lower carbon efficiency. Therefore, improving the refining step and chemical integration may be a good option.

The carbon dioxide emissions come from both direct burning of fuel to provide energy for the processes and indirect  $CO_2$  emissions derived from utility consumption. The  $CO_2$ emissions of the four routes are shown in Table 12. Taking the PMTO route as an example, the direct and indirect  $CO_2$ emissions are 0.15 t  $CO_2/t$  olefin, and 0.40 t  $CO_2/t$  olefin,

	Table 1	12. ]	Input	and	Output	of	Four	Routes
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item	PFTO	PZTO	РМТО	РРТО
input				
plastic (t/t olefin)	3.70	1.48	1.05	2.09
electricity (GJ/t olefin)	42.98	52.11	49.84	76.50
steam (GJ/t olefin)	16.04	6.40	6.50	10.44
total energy use (GJ/t olefin)	160.15	98.85	84.89	100.01
output				
ethylene (t/t olefin)	0.14	0.13	0.58	0.58
propylene (t/t olefin)	0.25	0.23	0.37	0.30
butylene (t/t olefin)	0.61	0.64	0.05	0.11
$CO_2$ emissions (t/t olefin)	3.48	1.21	0.55	0.69
product energy (GJ/t olefin)	47.00	47.00	47.00	47.00
energy efficiency (%)	29.35%	47.55%	55.60%	47.21%

respectively. The PMTO route would achieve almost near net zero carbon emissions if all of the utility energy consumption comes from renewable sources. Based on the carbon content of the mixed plastic waste, it would release 3.5 tons of carbon dioxide to burn waste plastics. Therefore, the potential reduction  $CO_2$  emissions is 2.95 t  $CO_2/t$  olefin using the chemical cycling method compared to that of incineration.<sup>64</sup> In addition, the conversion of waste plastics into light olefin pathways can reduce fossil resources. Approximately, 3.8 t of coal or 3.86 t of crude oil would be saved once light olefins were produced from waste plastics instead of fossil resources.<sup>82</sup> The chemical cycling of waste plastics to light olefins not only produces high-valued light olefins but also reduces environmental pollution and carbon emissions, which are green and eco-friendly.

**3.3. Energy Efficiency.** Based on literature data<sup>28,42,47</sup> and simulation results, the yields of light olefins in PFTO, PZTO, PMTO, and PPTO were respectively 26.99, 67.68, 95.61, and 47.87%. To produce one ton of light olefins, it would consume about 3.70, 1.48, 1.05, and 2.09 tons of MPW as shown in Table 12, respectively.

In the PFTO, the energy efficiency and  $CO_2$  emissions were respectively 29.35% and 3.48 t  $CO_2/t$  olefin, which were inferior to those of the PMTO with 55.60% and 0.55 t/t olefin. The low olefin selectivity and high  $CO_2$  selectivity result in the high energy consumption and  $CO_2$  emissions in PFTO. For the PMTO, light olefin selectivity was up to 96% in the MTO unit. According to ref 28, the newly developed OX-ZEO catalyst improved the light olefin selectivity. olefin selectivity



Figure 12. Carbon flow of life cycle assessment.

could be increased to 80% in the PZTO route. The energy efficiency and CO<sub>2</sub> emissions were 47.55% and 1.21 t CO<sub>2</sub>/t olefin in PZTO. This means that raising olefin selectivity can reduce raw material consumption and CO<sub>2</sub> emissions. For the PPTO, the energy efficiency and CO<sub>2</sub> emissions were 47.21% and 0.69 t of  $CO_2/t$  olefin. In the energy efficiency aspect, the PZTO was roughly equivalent to that of the PPTO, while the PMTO shows the much better performance in  $CO_2$  emissions and energy efficiency. Therefore, the energy efficiency in waste plastics to olefins is much higher than that of CTO (36.1%) and nature gas to olefins (NGTO) (52.2%).42,83 From the point of view of elemental composition, waste plastics are mainly composed of two elements, carbon and hydrogen, and compared with coal, waste plastics have more advantages. From the perspective of process flow, the PMTO route process is shorter than the conventional coal-to-olefins route; especially the AGR unit and WGS unit are cut out in the PMTO route. Additionally, the improved carbon utilization and higher light olefin selectivity increase the yield of light olefins, which indirectly improves the energy efficiency of PMTO.

3.4. Economic Performance. In this section, the equipment cost was calculated based on the disposal scale of waste plastic of  $30 \times 10^4$  t/y in a commercial plant. The plant operation time was assumed to be 8000 h per year.<sup>84</sup> The economic analysis, including fixed-capital investment (FCI), product cost, net present value (NPV), internal rate of return (IRR), net profit, and payback period (PBP), was performed and discussed.

According to the industrial scale simulations, 37,500 kg/h of MPW and 46875 kg/h of water need to enter the pyrolysis reactor as raw materials and 84374.55 kg/h of syngas is produced. In total, 20810.67 kg/h of ethylene and 13431.48 kg/h of propylene can be produced through the unit operation of methanol synthesis and MTO in the PMTO route. The product cost of light olefins from waste plastics is estimated to be 4918.59 CNY/t olefin for the PMTO route, compared to 5400.23 CNY/t olefin for PZTO, 6003.36 CNY/t olefin for PFTO, 6763.13 CNY/t olefin for PPTO, and 6400 CNY/t olefin for CTO.72,83 Production costs consist of seven components, namely raw material, utilities, operation and maintenance, distribution and selling, plant overhead, administration, and depreciation, which can be calculated based on the ratio factor as shown in Figure 13.42 As can be seen, the PMTO route has a much better performance as far as the product cost is concerned.

The main product costs are contributed by the raw materials and utilities in the PFTO route. The utilities contribute to the main product cost per ton of light olefins in the PMTO process, which accounted for 78.92%. It implies that the product cost of PMTO can be readily reduced by employing high-quality catalyst to reduce reaction temperature and increase the heat recovery system. The raw materials hold second place in the product cost. The major parameters for the discounted cash flow analysis are shown in Table 13.

The price of waste plastics is much lower (i.e., 400 CNY/t) in China compared to that in the developed countries.<sup>18</sup> Noticeably, it can be beneficial to turn waste plastics into highvalued products, and if the government can subsidize these enterprises, it would be of great help to the endeavors. Fixedcapital investment (FCI), net profit, payback period, NPV, and IRR of plants are shown in Table 14.

The financial study results show that the PMTO route has the lowest product cost (4918.59 CNY/t olefin) and higher

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internal rate of return (i.e., 70.18%) compared to the other three routes. The payback period and net profit of the plant are 1.87 years and 99008.20  $\times$  10<sup>4</sup> CNY, respectively. In the route of making gasoline and diesel from waste plastics,<sup>18</sup> the payback period was 3 years with the total annual profit of  $51053.21 \times 10^4$  CNY (exchange rate is 7) and an IRR of 35.69%. Compared with the waste plastic to gasoline and diesel route, PMTO has great advantages in terms of net profit, return period, and internal rate of return. From the perspective of economic performance, the PMTO route is featured by less FCI, a shorter payback period, and a higher net profit. Therefore, the PMTO route has the best economic performance among all four routes discussed above.

3.5. Sensitivity Analysis. We conducted sensitivity analysis to understand which factors have the biggest impact on product costs.<sup>82</sup> By doing so, we can develop effective targeted measures to reduce production costs and increase corporate profits. Sensitivity analysis was performed on four parameters, which were raw material prices, scale, utilities, and operating and maintenance costs. In sensitivity analysis, we examine to what extent one parameter affects the production costs while keeping the other three dimensions as the baseline values. The factors that most affect the production costs can be discovered through sensitivity analysis, following which the corresponding measures can be taken to improve its economic performance. Figure 14 shows a sensitivity analysis of four dimensions in four light olefin production routes.

As the utility dimension changes by  $\pm 20\%$ , the product costs vary by  $\pm 10.63$ ,  $\pm 15.40$ ,  $\pm 15.78$ , and  $\pm 13.07\%$  for PFTO, PZTO, PMTO, and PPTO routes, respectively. Meantime, if the operating and maintenance costs dimension changed by  $\pm 20\%$ , the product costs only changes by  $\pm 1.42$ ,  $\pm 0.63$ ,  $\pm$ 0.60, and ±1.41% for PFTO, PZTO, PMTO, and PPTO routes, respectively. Hence, enhancing both workers' wages and their welfare benefits, as well as intensifying equipment maintenance and repair, is not expected to exert a substantial influence on production costs. Suppose that the scale dimension changes by  $\pm 20\%$  and the product costs for PFTO, PZTO, PMTO, and PPTO routes change by  $\pm 5.55$ ,  $\pm$ 3.02,  $\pm$  3.14, and  $\pm$ 5.57%, respectively, it implies that increasing the disposal scale of waste plastics can reduce production costs, especially for PPTO routes, as shown in Figure 14. The utility dimension is much more sensitive than

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#### Table 13. Parameters for the Discounted Cash Flow Analysis

description	PFTO	PZTO	РМТО	РРТО
fixed-capital investment ( $\times 10^4$ CNY/y/t olefin)	1.48	0.59	0.50	1.70
product cost (CNY/t olefin)	6003.36	5400.23	4918.59	6763.13
project builds cycle (year)	5	5	5	5
capital investment (×10 <sup>4</sup> CNY/Y)	31,200	31,200	37,000	63,600
annual income (year)	70282.39	176857.59	240093.81	121646.26

### Table 14. Economic Performance for MPW to Light Olefins<sup>56,57</sup>

description	PFTO	PZTO	РМТО	РРТО
fixed-capital investment ( $\times 10^4$ CNY/y/t olefin)	1.48	0.59	0.50	1.70
product cost (CNY/t olefin)	6003.36	5400.23	4918.59	6763.13
annual revenue (×10 <sup>4</sup> CNY/Y)	70282.39	176857.59	240093.81	121646.26
net profit (×10 <sup>4</sup> CNY/Y)	21664.72	67219.21	99008.20	24513.33
payback period (year)	7.20	2.32	1.87	12.97
NPV ( $\times 10^4$ CNY)	139282.76	724212.01	1106568.75	31620.48
internal rate of return (%)	44.56%	61.31%	70.18%	25.24%





that of the raw material prices and operating and maintenance costs in the four routes. Therefore, using more advanced technology to reduce the electricity and steam consumption in utilities will effectively improve economic performance of waste plastics to olefins.

#### 4. CONCLUSIONS AND OUTLOOK

-10

Waste plastics have become the second biggest environmental concern following climate change. Chemical cycling of waste plastics into light olefins plays an important role in the circular economy and closed-loop recycling of plastics. In this work,

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four potential technical routes, that is, PFTO, PZTO, PMTO, and PPTO, have been studied. The carbon footprint, energy efficiency, and economic performance were analyzed based on techno-economic evaluation and life cycle assessment. The results demonstrated that the overall carbon efficiency of the PFTO, PZTO, PMTO, and PPTO routes was about 26.61, 67.59, 95.49, and 47.81%, respectively. The PMTO route had the advantage of the highest carbon efficiency in the four routes. The energy efficiency and CO<sub>2</sub> emissions of PMTO were 55.60% and 0.55 t/t olefin, respectively, better than the other three routes with PFTO of 29.35% and 3.48 t/t olefin, PZTO of 47.55% and 1.21 t/t olefin, and PPTO of 47.21% and 0.69 t/t olefin. The product cost of PFTO, PZTO, PMTO, and PPTO routes was about 6003.36, 5400.23, 4918.59, and 6763.13 CNY/t olefin, respectively. It is shown that the cost of waste plastics to olefins is much more sensitive to the utility expense than to raw material prices and operating and maintenance costs in the four routes. Thus, it is expected that reducing the utility cost will be more effective in improving the overall economic performance of waste plastics to olefins based on the sensitivity analysis. As shown, PMTO is the most promising route in terms of performance. In fact, the methanol-to-olefins process has already been commercialized, which makes PMTO the potential approach for large-scale cycling of waste plastics in the near future.

#### ASSOCIATED CONTENT

#### Data Availability Statement

The data used to support the findings of this study are available from the corresponding author upon request.

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#### **Author Contributions**

J.L.: conceptualization, methodology, investigation, writingoriginal draft, writing-review, and editing. D.L.: conceptualization, resources, funding acquisition, writing-review, and editing. S.X.: investigation, writing-review, and editing. M.Y.: conceptualization, project administration, funding acquisition, supervision, writing-review, and editing.

#### Notes

The authors declare no competing financial interest.

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#### ■ NOMENCLATURE

AGR	Acid Gas Removal
CG	Coal Gasification
СТО	Coal-to-olefins
DMTO	Dimethyl ether/Methanol-to-olefins
E-LCA	Economic Life Cycle Assessment
FCC	Fixed-Capital Cost
FCI	Fixed-Capital Investment
FTO	Fischer-Tropsch-to-olefins
IRR	Internal Rate of Return
LCA	Life Cycle Assessment
MPW	Mixed Plastic Waste
MS	Methanol Synthesis
MTO	Methanol-to-olefins
NGTO	Natural Gas-to-olefins
NPV	Net Present Value
OS	Olefins Selectivity
OX-ZEO	Oxide-zeolite
PBP	Payback Period
PE	Polyethylene
PET	Polyethylene Terephthalate
PFTO	Plastic-based Fischer—Tropsch-to-olefins
PMTO	Plastic-based Methanol-to-olefins
PP	Polypropylene
PPTO	Plastic-based Pyrolysis Oil to Olefins
PS	Polystyrene
PtH	Power to Hydrogen
РТО	Plastic-to-olefins
PVC	Polyvinyl Chloride
PZTO	Plastic-based OX-ZEO Process to Olefins
ROR	Rate of Return
S/CH	Steam/Hydrocarbon
S/P	Steam/Plastics
SC	Steam Cracking
STO	Syngas to Olefins
TCI	Total Capital Investment
TPC	Total Production Cost
WGS	Water–gas Shift

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