Integrated Assessment of Waste Tire Pyrolysis and Upgrading Pathways for Production of High-Value Products

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ABSTRACT: Waste tire pyrolysis has received increasing attention as a promising technology recently due to the shortage of fossil resources and the severity of environmental impact. In this study, the process of waste tire pyrolysis and upgrading to obtain high-value products was simulated by Aspen Plus. Also, based on life cycle assessment, the indexes of energy, environmental, economic, and comprehensive performance were proposed to evaluate different high-value pathways. Results demonstrate that the integrated system of waste tire pyrolysis, pyrolytic oil (TPO) refining, and pyrolytic carbon black (CBp) modification has higher energy efficiency than the independent system of TPO refining, with an improvement rate of 2.6%. Meanwhile, the resource-environmental performance of the integrated system is better. However, combined with the economic benefit, the independent system is more comprehensively beneficial, with the index of comprehensive performance (BEECR) of 0.94, which increases by 3.3% compared with the integrated system. Furthermore, the comparisons of different improved high-value paths based on the independent system as the benchmark indicate that the pathway of promoting sulfur conversion during pyrolysis to reduce the sulfur content in TPO can increase the BEECR from 0.94 to 1.064, with the growth of 13.2%. Also, the physical modification of CBp to reduce the production cost and environmental impact has better performance of BEECR, increasing by 20.2%. The final sensitivity analyses show that the combined improved high-value case established by the abovementioned two paths can achieve a favorable benefit in a wide range of crude oil and waste tire prices and the environmental tax.
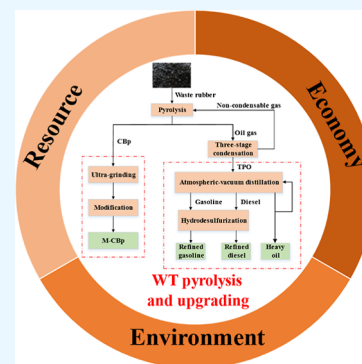
1. INTRODUCTION

With the rapid development of the automobile industry, about 1.4 billion used tires were regarded over the world annually.[1] It was predicted that the number of waste tires (WTs) would exceed 1.6 billion in 2024,[2] and the increase would reach 20% by 2030.[3] Various economic and environmental problems were aggravated due to the increasing quantity of WTs and inappropriate recycling methods in the long term.[4−7] Therefore, it is significant for WT disposal to explore effective, profitable, and environmentally friendly methods.

Pyrolysis was considered the most prevalent, attractive, and environmentally friendly among WT thermal conversion technologies owing to the advantages of faster reduction, less environmental pollution, and higher economic benefits.[2,8−11] However, there were some shortcomings of pyrolysis products. For tire pyrolytic oil (TPO), drawbacks of high sulfur content and viscosity, low flash point and cetane number, and impurity restricted its direct utilization.[12−17] With regard to pyrolytic carbon black (CBp), it was possible to be used as reinforcing filler and pigment in rubber and the precursor of activated carbon.[18,19] Nevertheless, CBp's intrinsic drawbacks, including high ash and sulfur content, poor micropore structure, and carbonaceous residues on the surface, still hindered its direct utilization.[1,20,21] As mentioned above, to improve the economic performance of pyrolysis process, the upgrading of TPO and CBp was necessary.

To obtain the clean liquid products, the researchers actively developed the different desulfurization methods of TPO, including in situ and ex situ desulfurization. In situ desulfurization referred to the direct removal of organic sulfur in TPO through additives during the pyrolysis (such as NaOH, Ca(OH)$_2$, Na$_2$CO$_3$, CaO, and zeolite).[22−26] Generally, the in situ desulfurization efficiency was not ideal. Meanwhile, it was difficult for additives to separate from the pyrolytic solid product. By contrast, ex situ desulfurization was more effective than in situ desulfurization but more expensive owing to additional desulfurization equipment.[27] Hydrodesulfurization (HDS) was a traditional method of ex situ desulfurization, and the most commonly used to fulfill the sulfur removal of oil products. The experimental results of HDS under different catalysts and parameters demonstrated that the maximum removal efficiency could reach 99.9%.[28,29] Different from sulfides without ring structure, dibenzothiophene (DBT) and substituted DBTs were more difficult to be removed through
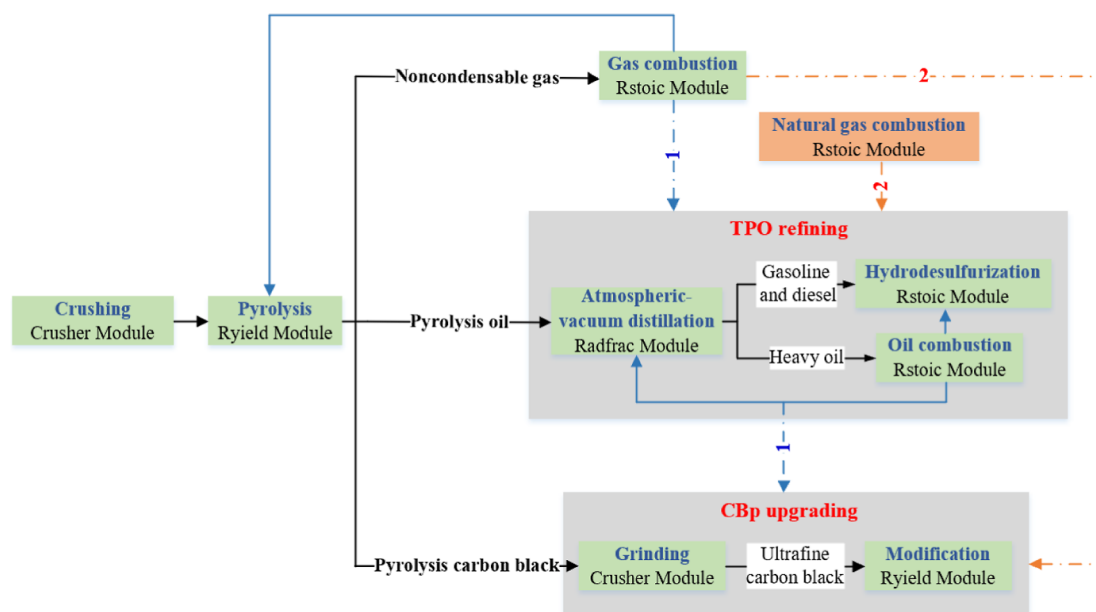
Figure 1. Process flowsheet of basic high-value cases of WT pyrolysis.

HDS owing to the influence of steric resistance.[29,30] Despite all this, other methods of ex situ desulfurization were unable to achieve the same efficiency as HDS, although some disadvantages of HDS could be eliminated.[31,32]

With respect to CBp upgrading, modification and activation were adopted according to different utilization purposes. CBp activation aimed at increasing the surface area and porosity to obtain activated carbon with excellent adsorption performance, while the target of CBp modification was to make modified carbon black (M-CBp) equal to commercial carbon black.[33,34] The surface area of activated CBp could be greater than 400 m^2/g, even in excess of 700 m^2/g in some researches, which was almost equal to that of commercial activated carbon.[35–40] With regard to CBp modification, pickling was a traditional method that could effectively remove ash and sulfur. It could make M-CBp achieve the same performance as commercial carbon black. Various acids (such as HCl, HF, H_2SO_4, HNO_3, and the mixture of acids) were applied to experimental studies.[19,41–43] However, the high cost and indirect environmental impact of acids and the secondary pollution of acid-based liquid waste were the deficiencies of pickling. For the abovementioned reasons, simple physical modification could be adopted to reduce the environmental-economic impact of CBp modification. This method, only including grinding, washing, and screening steps, could generate M-CBp, which was able to substitute at least 30% of commercial carbon black.[44,45]

To sum up, it is economically beneficial for pyrolytic products to be further upgraded, but the environmental-economic performances of upgrading technologies still need comparative evaluations.

Life cycle assessment (LCA) has been frequently applied to the evaluation of different WT treatment technologies.[46–50] The previous studies on LCA of WT pyrolysis focused on the comparative analysis with other treatment methods, from the perspective of material and energy flow analysis,[51] economic analysis,[52,53] environmental analysis,[54,55] and integrated analysis.[56,57] Results showed that pyrolysis was an eco-effective method. In our previous research, the environmental-economic comparison between conventional pyrolysis and a single high-

value pyrolysis pathway was analyzed. Results indicated that the upgrading of pyrolytic products played a significant role in improving the environmental-economic performance of WT pyrolysis.[58]

It could be found that the previous reports only focused on the comparison of different treatment technologies of WTs. However, the influence of various solid-phase and liquid-phase upgrading methods on the whole pyrolysis system was hardly concerned. Therefore, to find an optimal path for WT pyrolysis and upgrading, this study aimed to investigate the resource, environmental, and economic performances of WT pyrolysis and upgrading to obtain high-value products. Two basic high-value schemes of WT pyrolysis were proposed and compared based on Aspen Plus simulation and LCA method. Concurrently, based on a better basic case, the comprehensive performances of improved high-value pathways, including different CBp modification and TPO refining methods, were further explored to identify the optimum improved pathway.

2. SIMULATION AND ASSESSMENT METHODS

2.1. Aspen Plus Simulation. *2.1.1. Process Description.* The basic high-value process of WT pyrolysis was mainly divided into several parts: pretreatment, pyrolysis and gas combustion, TPO refining, and CBp upgrading. The concrete process was as follows. First, WT rubber was crushed to obtain rubber particles with appropriate size. Then, rubber particles were decomposed in the pyrolysis reactor. Next, non-condensable gas separated from the gaseous product was used as fuel. Meanwhile, TPO was further refined to obtain refined oil products, and CBp was modified to obtain upgraded carbon black by pickling.

2.1.2. Simulation Objective. Two basic schemes: integrated system of waste rubber pyrolysis, TPO refining, and CBp modification (Case 1) and independent system of TPO refining (Case 2) were designed. The independence mentioned here meant that TPO could be transported to the oil refinery for centralized treatment rather than combined upgrading with other pyrolytic products. Waste heat utilization as much as possible was considered in Case 1, while Case 2 was more
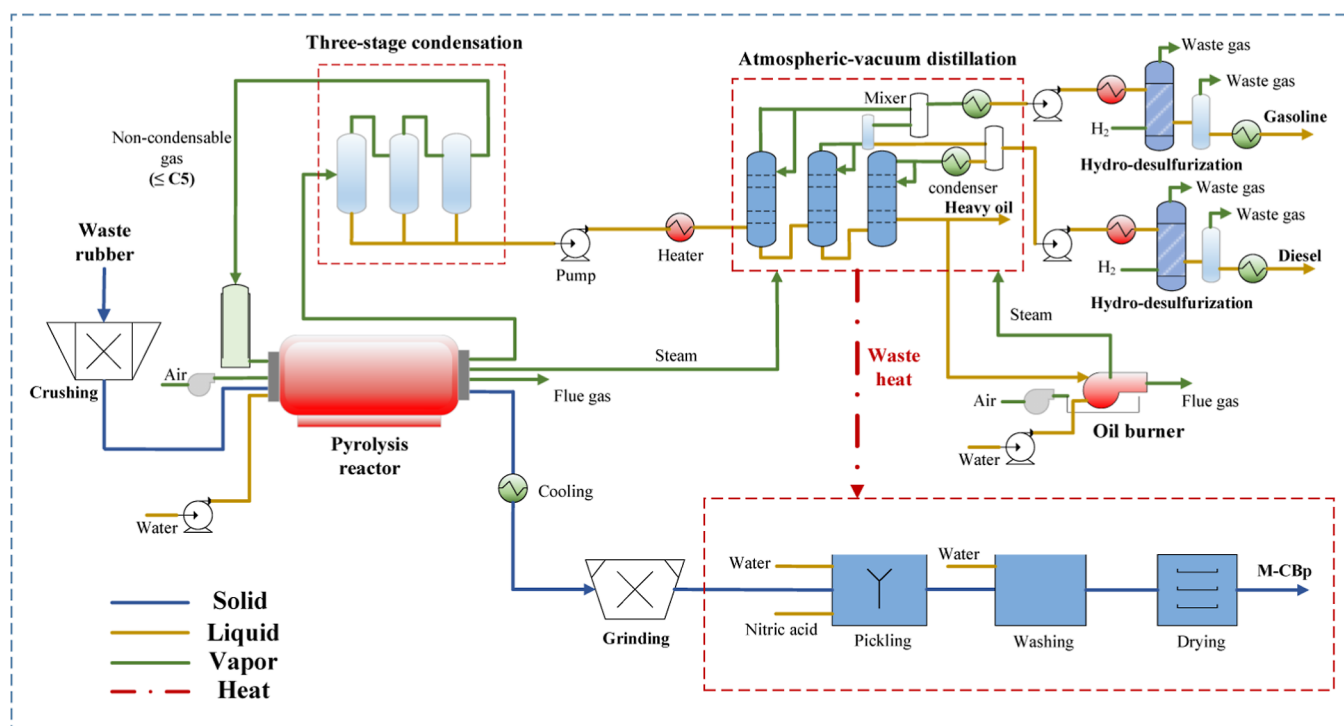
(a) Case 1
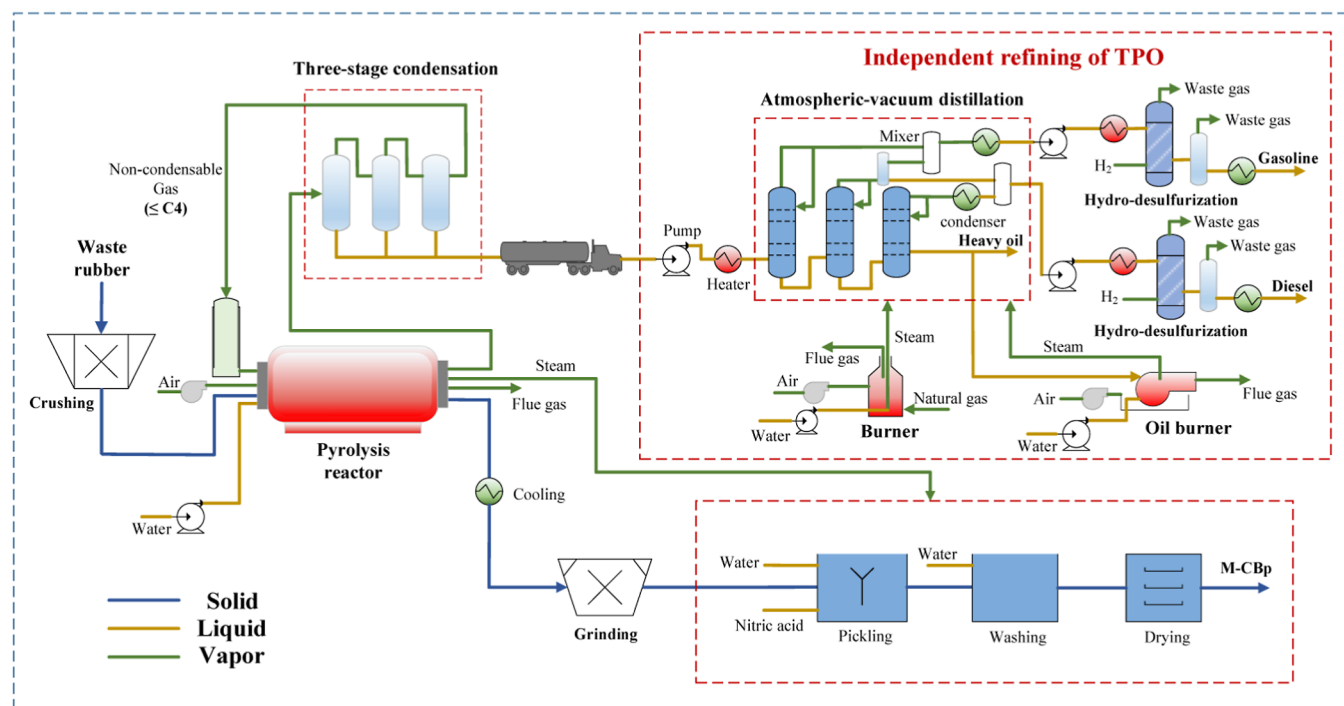
(b) Case 2

Figure 2. System charts of two basic high-value cases of WT pyrolysis: (a) Case 1 and (b) Case 2.

inclined to the flexibility of plant construction. The path of energy utilization during simulation is shown in Figure 1. In Case 1: energy of non-condensable gas combustion was used for pyrolysis and TPO refining. To satisfy the heat demand of TPO

refining and minimize the resource input, part of heavy oil (HYO) obtained from fraction cutting was used as fuel to generate the steam needed in TPO refining. Meanwhile, part of low-quality steam produced from waste heat in the atmospheric-

Table 1. Proximate and Ultimate Analyses of WT Rubber, CBp, and M-CBp

	volatile matter	fixed carbon	Ash	C	H	O	N	S
	proximate analysis (wt %, db)			ultimate analysis (wt %, db)				
WT rubber	60.05	33.84	6.11	83.07	6.48	1.95	0.47	1.92
CBp	5.1	80.75	14.15	79.43	0.38	2.03	0.54	3.47
M-CBp	2.90	93.61	3.49	90.72	0.47	2.50	0.67	2.15

Table 2. Operation Parameters of Main Simulation Units

part	unit	operation parameter	yield and conversion rate
pyrolysis	pyrolysis reactor	450 °C, 101.075 kPa	9.1% (gas)
			43.2% (solid)
			47.7% (liquid)
	combustion of non-condensable gas	900 °C, 1 atm	
	primary distillation tower	185 °C, 0.38 MPa	
	atmospheric tower	380 °C, 0.25 MPa	
	vacuum tower	430 °C, 0.1225 MPa	
TPO refining	gasoline desulfurization	300 °C, 2.5 MPa, H$_2$/oil = 400	100% of C$_6$H$_6$S and C$_6$H$_{14}$S$_2$
			95.5% of C$_5$H$_6$S
	diesel desulfurization	360 °C, 5 MPa, H$_2$/oil = 600	99.7% of benzothiophene
	combustion of vapor and liquid fuels	900 °C, 1 atm	
CBp upgrading	two-stage grinding	outlet particle size D50 = 1 mm (first)	100%
		outlet particle size D50 = 0.05 mm (second)	100%
	CBp modification (pickling)	60 °C, 1 atm	80% of ash removal
			49.77% of sulfur removal
			5.86% of carbon loss

vacuum distillation unit provided the energy of CBp modification, and the rest of it was considered as the by-product. In Case 2: energy provided by non-condensable gas in TPO refining was replaced with natural gas. In addition to the pyrolysis unit, non-condensable gas was also used for CBp modification.

2.1.3. Simulation Modules. Based on Aspen Plus, pyrolysis processes of WTs for high-value products were simulated to obtain the mass flow and energy flow. As shown in Figure 1, both the crushing of WT rubber and ultra-grinding of CBp adopted the Crusher module. The crushing process was divided into three steps, and the types of crushers were selected as JAW, JAW, and CONE, respectively. The combustion of non-condensable gas, HYO and natural gas, and the HDS of gasoline and diesel adopted the Rstoic module. The Ryield module was applied to the pyrolysis reactor and CBp modification unit. Specially, the Radfrac module was a rigorous model for simulating multistage gas–liquid distillation, which was applied to the atmospheric-vacuum distillation of TPO. The system charts for the simulation are shown in Figure 2.

2.1.4. Simulation Parameters. 2.1.4.1. Model Parameters. A plant with the scale of 11 t/h WTs with steel wire stripped was simulated, in which the WT was defined as a non-conventional material. In the simulation, waste passenger tires were taken as the objective. WT rubber was then crushed into the particles with the D50 of 6 mm after simple cutting to guarantee the uniformity of particle size during pyrolysis. The proximate and ultimate analyses of the WT rubber are presented in Table 1. To ensure the data reasonability, five samples of every substance were randomly taken for test, and the average value was considered as the analysis result. As the atmospheric-vacuum distillation of TPO was similar to the petroleum rectification process, "RK-SOAVE", a special property method for petroleum processing, was applied as the basic method in the simulation of the present work.

2.1.4.2. Operation Parameters. The operation parameters of main units in the process of simulation (Figures 1 and 2) are summarized in Table 2. Main simulation parameters are taken from the experimental data of our project. Specially, the parameter of pickling was referred to the data of literature.[59] In TPO refining, the unit of atmospheric-vacuum distillation consisted of primary distillation tower, atmosphere tower, and vacuum tower, and the sulfur contents of light fraction and medium fraction in TPO were 3160 and 9475 ppm, respectively. Low-sulfur gasoline and diesel could be obtained through hydrodesulfurization.

The composition of non-condensable gas obtained from pyrolysis is listed in Table S1 in Supporting Information. The components of TPO obtained from the experiment were replaced with modeling compounds between C$_8$ and C$_{30}$,[60] according to the distillation data of the real boiling point of TPO and the group components of gasoline and diesel in the experiment, which are summarized in Tables S2 and S3, and the yield of modeling compounds is listed in Table S4.

2.2. Life Cycle Assessment (LCA). The evaluation method of LCA in this study is CML-IA baseline V3.05/World 2000 provided by LCA software SimaPro. Ten kinds of resource and environmental indexes were taken into consideration in this evaluation, including abiotic depletion potential (ADP) (mineral), ADP (fossil), global warming potential (GWP), ozone layer depletion potential (ODP), human toxicity potential (HTP), freshwater aquatic eco-toxicity potential (FAETP), terrestrial eco-toxicity potential (TETP), photo-chemical oxidation potential (POCP), acidification potential (AP), and eutrophication potential (EP).

2.2.1. Goal and Scope. Waste disposal processes (end-of-life cycle) were discussed in this study, starting from WTs at the recycling plant and ending up with products completely upgraded. An optimal improved high-value pathway was obtained by the comprehensive comparison of different
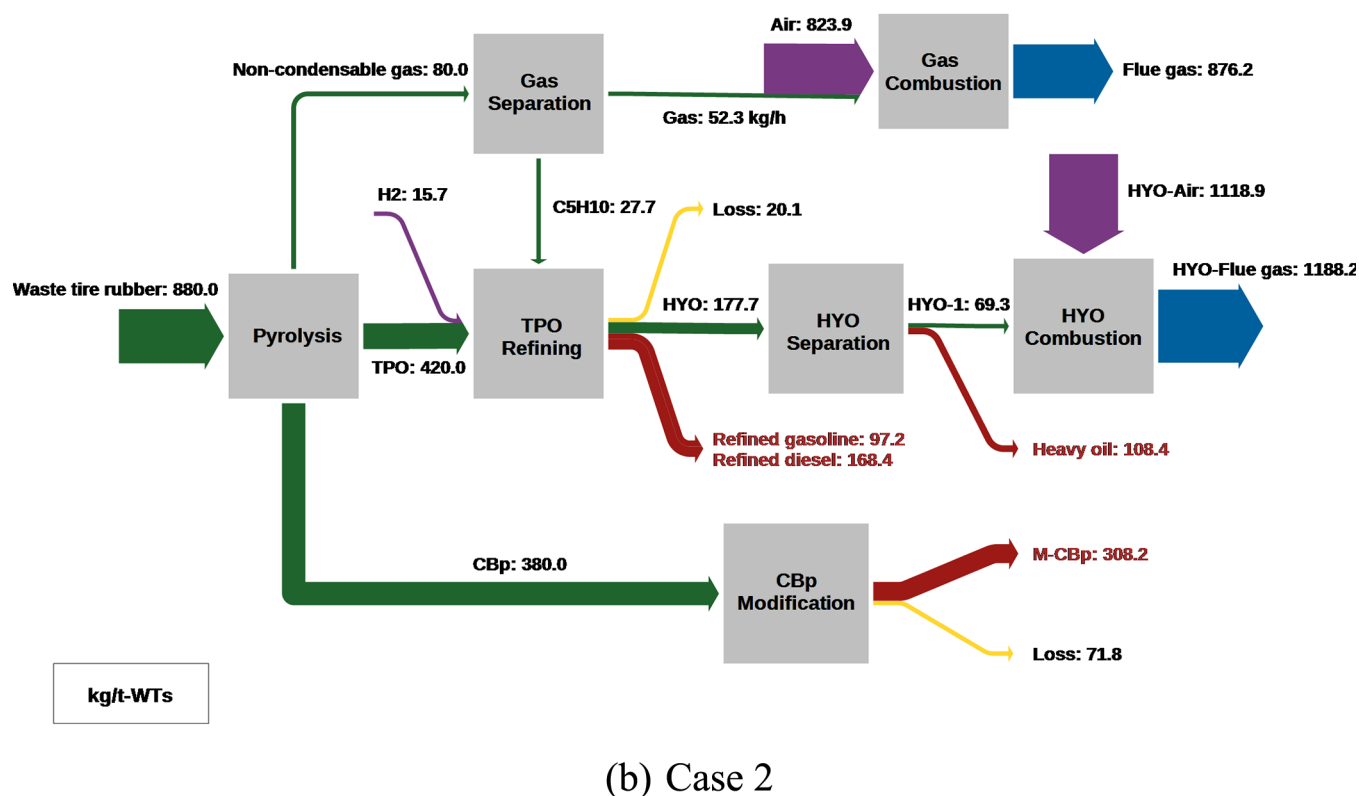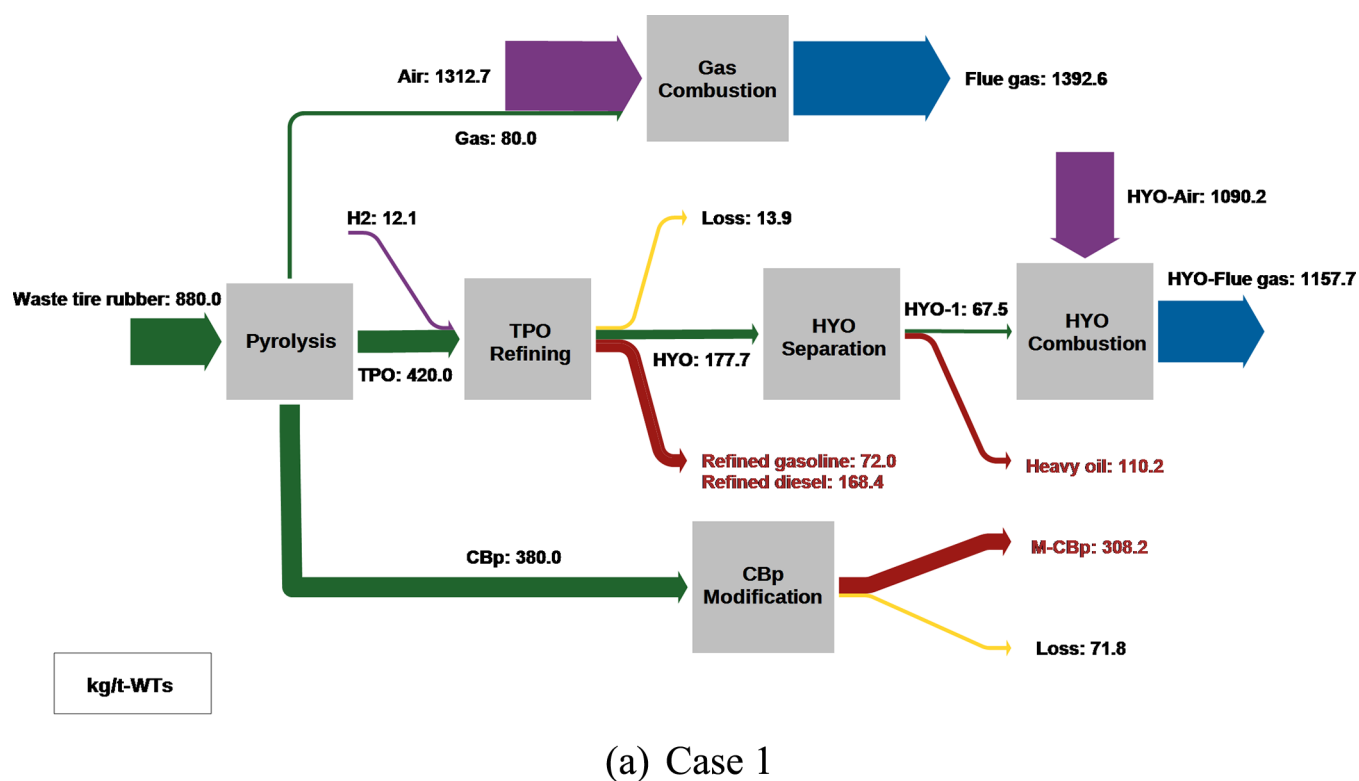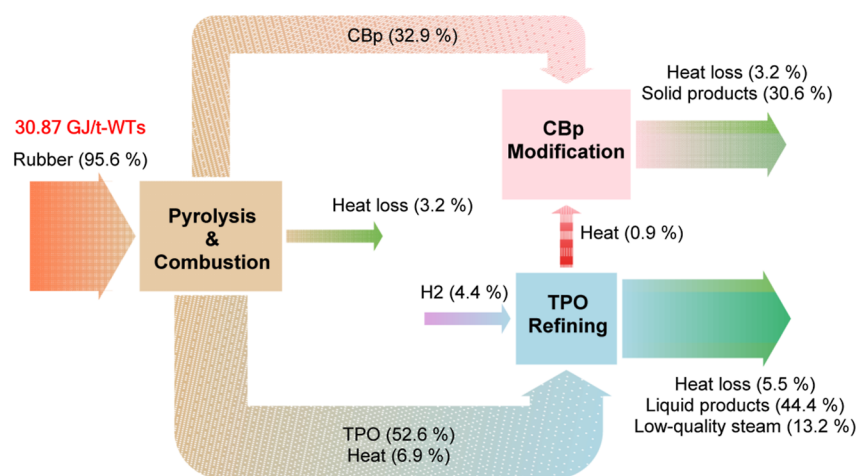
(a) Case 1

(b) Case 2

Figure 3. Material flows of two basic high-value cases of WT pyrolysis: (a) Case 1 and (b) Case 2.

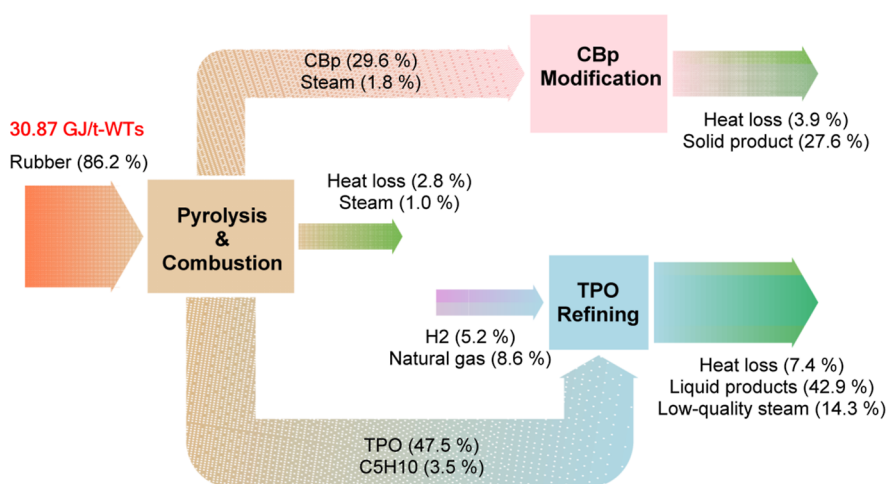upgrading paths. The functional unit of this assessment was 1000 kg WTs.

2.2.2. Evaluation Methods. 2.2.2.1. Energy Utilization Index. To analyze the energy consumption of two basic high-value cases of WT pyrolysis, energy recovery efficiency (ERE),

an energy utilization index was incorporated into the evaluation, as shown in eq 1

$$ERE = \frac{EUE}{TIE}$$

(1)

(a) Case 1

(b) Case 2

Figure 4. Energy flows of two basic high-value cases of WT pyrolysis: (a) Case 1 and (b) Case 2.

where EUE and TIE represent effective utilization energy and total input energy, respectively.

2.2.2.2. Index of Resource and Environmental Impacts. To evaluate the resource and environmental impacts between different improved high-value paths of WT pyrolysis, the emission reduction rate (ERR) was defined as the relative percentage change from the standardized value (SV) of the improved path to that of the basic case in eq 2.

$$ \text{ERR} = \frac{\text{SV}_{\text{Improved path}} - \text{SV}_{\text{Basic case}}}{\text{SV}_{\text{Basic case}}} \times 100\% \tag{2} $$

2.2.2.3. Economic Performance Index. To evaluate the economic performances of different cases, the benefit to cost ratio (BCR) was established. As shown in eq 3, it represents the ratio of the product benefit to the production cost. The production cost includes raw material cost, utilities, equipment depreciation cost, maintenance cost, insurance premium, employee salary and welfare, bank loan interest, management cost, and other related expenses.[58,61,62]

$$ \text{BCR} = \frac{\sum P_j \times M_j}{C^p} \tag{3} $$

where P_j represents the price of product j, CNY/t; M_j represents the yield of product j, t/t−WTs; and C^p represents the production cost, CNY/t−WTs.

2.2.2.4. Comprehensive Performance Index. Based on BCR, the environmental influence was further considered, and the index of comprehensive performance (BEECR) was defined as the ratio of the product benefit to the total environmental-economic cost, as shown in eq 4

$$ \text{BEECR} = \frac{\sum P_j \times M_j}{C^p + C^e} \tag{4} $$

where C^e represents the environmental cost, CNY/t−WTs.

According to the considered environmental indexes, some important and critical pollutants were considered, including 16 kinds of air pollutants (CO_2, CH_4, CO, N_2O, NOx, HCl, H_2S, NMVOC, PM_{10}, SO_2, benzene, acetaldehyde, toluene, xylene, formaldehyde, and benzopyrene), 8 kinds of water pollutants (ammonia nitrogen, benzene, COD, 1,2-dichlorobenzene,
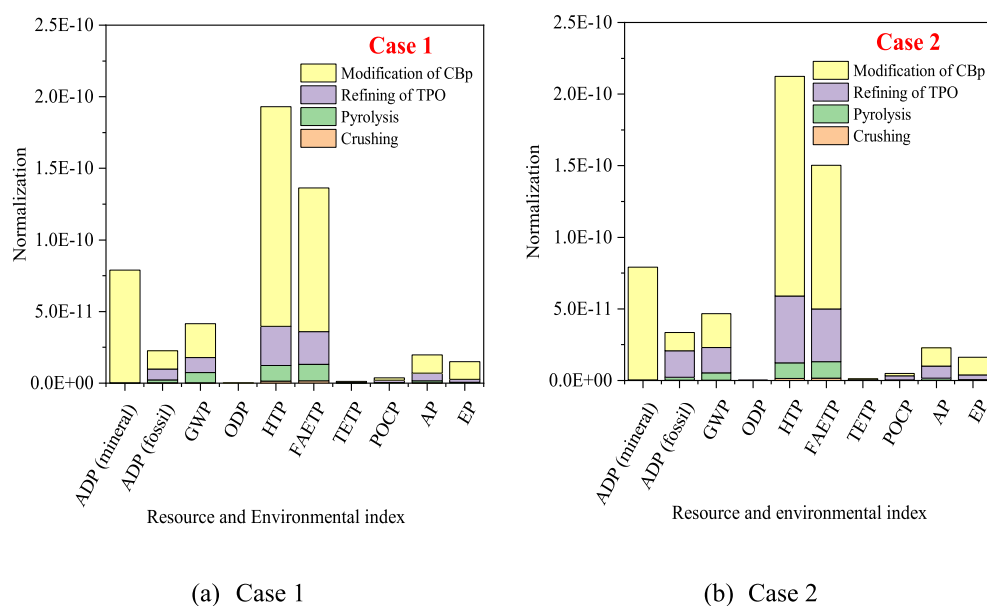
Figure 5. Resource and environmental impacts of two basic high-value cases of WT pyrolysis: (a) Case 1 and (b) Case 2.

ethylbenzene, toluene, xylene, and phenol), and solid waste. The environmental tax of pollutants was based on the prescribed average value of the Environmental Protection Tax Law of China (Revised in 2018).[58]

2.2.2.5. Sensitivity. To investigate the influence of different factors, the sensitivity of an indicator was discussed. As shown in eq 5, it represents the change in the indicator caused by the change of a factor. The larger the sensitivity value, the greater the impact of the factor.

$$SA_x = \left| \frac{\Delta EO_y}{\Delta V_x} \right| \times 100\% \tag{5}$$

where ΔEO_y represents the variation of the indicator value; and ΔV_x represents the variation of the factor.

3. RESULTS AND DISCUSSION OF TWO BASIC HIGH-VALUE CASES OF WT PYROLYSIS

3.1. Material Flow Distribution. From the perspective of rubber fraction recycling, material flows of Case 1 and Case 2 were obtained based on simulation results. As shown in Figure 3, 880 kg/t−WTs crushed rubber in Case 1 is converted into 72 kg/t−WTs refined gasoline, 168.4 kg/t-WTs refined diesel, 110.2 kg/t−WTs heavy oil, and 308.2 kg/t−WTs M-CBp. As for Case 2, C_5 component from non-condensable gas is incorporated into TPO, so that the yield of refined gasoline rises to 97.2 kg/t−WTs, increasing by 34.7% relative to that of Case 1. Due to the difference of energy utilization, the fraction of HYO for combustion is slightly higher than that of Case 1, resulting in a slight decline in the yield of heavy oil. It can be observed that compared with the experimental studies on tire pyrolysis,[63−65] the yields of three-phase products in WT pyrolysis are 38−60 wt % (liquid), 27−42.5 wt % (solid), and 2.5−27 wt % (gas), respectively, which are within the appropriate scope.

3.2. Energy Flow Distribution. *3.2.1. Chemical Energy and Heat Energy.* As shown in Figure 4, the total energy input of Case 2 is 35.81 GJ/t−WTs, including three parts: WT rubber, natural gas, and hydrogen, accounting for 86.2, 8.6, and 5.2%, respectively. All low-quality steam produced from TPO refining

is treated as the by-product, which accounts for 14.3% of TIE. The heat loss of Case 2 is 14.1%, while the value of ERE is 85.9%. With regard to Case 1, there is no natural gas input owing to absolute energy utilization within the process. The total heat input of Case 1 is 32.3 GJ/t−WTs, and in detail the WT rubber and hydrogen account for 95.6 and 4.4%, respectively. The heat demand of CBp modification is provided by the partial waste heat of TPO refining, accounting for 0.9%. Then, the rest of low-quality steam accounting for 13.2%, is output as the by-product. Generally, the heat loss of the whole system is 11.9%, with ERE reaching 88.1%. Compared with Case 2, the ERE of Case 1 is higher because there is no chemical energy conversion process of natural gas combustion in Case 1.

3.2.2. Power Energy. The electricity consumptions of two cases are similar, with 365.3 kW h/t−WTs in Case 1 and 364.7 kW h/t−WTs in Case 2. The power consumptions of two cases are mainly concentrated in CBp modification unit and rubber pyrolysis unit, accounting for about 62 and 31%, respectively. In the pyrolysis unit, the electrical energy is mainly consumed by the rotary kiln and fans. The power consumption of CBp modification unit is due to the ultra-fine grinding of CBp and the hot air transmission in the drying process of M-CBp. The remaining power consumption includes the crushing of WT rubber before pyrolysis and the operation of pumps, fans, and other equipment in TPO refining.

3.3. Resource, Environmental, and Economic Impacts. *3.3.1. Resource and Environment.* Based on the simulation results of Case 1 and Case 2, the resource and environmental impacts of two cases were obtained (Figure 5). The energy utilization of Case 1 mainly adopts the system self-heating and the waste heat of its subunits, with little resource input. Therefore, the overall resource and environment load of Case 1 is better than that of Case 2. The largest environmental impact indicators of two cases are HTP, FAETP, and ADP (mineral). CBp modification is the most influential unit of these three indicators, accounting for 79.4, 73.6, and 99.7%, respectively, in Case 1, and 69.4, 62.4, and 99.5%, respectively, in Case 2. Subunits of CBp modification were discussed in detail. It is found that almost all of the load of ADP (mineral) comes from nitric acid added in the pickling process, accounting for 99.6%.
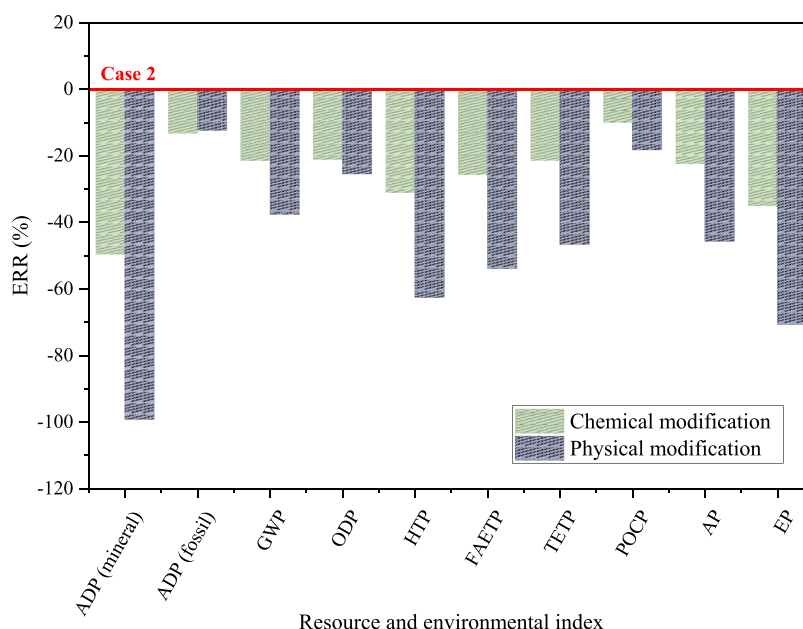
Figure 6. ERR of improved CBp modification paths.

Moreover, the main factor of HTP and FAETP is still nitric acid. Meanwhile, the electricity consumption during the drying process also results in a certain environmental impact on HTP and FAETP, accounting for about 14.3% and 23.3%, respectively.

Besides the abovementioned indicators, the high load was also generated in ADP (fossil) and GWP. CBp modification and TPO refining have great impacts on the two indicators in both cases. Among the total impact of ADP (fossil) in Case 1, CBp modification and TPO refining account for 56.3 and 34.0%, respectively. With regard to GWP, CBp modification and TPO refining account for 56.9 and 25.5%, respectively. As for ADP (fossil) in Case 2, CBp modification makes up 34.7%, with TPO refining accounting for 55.6%. With respect to GWP, CBp modification accounts for 48.4%, and TPO refining accounts for 38.1%.

The loads of ADP (fossil) and GWP caused by CBp modification in Cases 1 and 2 come from nitric acid and electricity. For TPO refining unit, the load of ADP (fossil) in Case 1 almost comes from activated carbon for hydrogen sulfide adsorption and removal, accounting for 94.8%. The load of GWP mainly comes from activated carbon and the direct emission of HYO combustion, which account for 49.9 and 48.2%, respectively. In Case 2: the load of ADP (fossil) mainly comes from activated carbon and natural gas, accounting for 57.3 and 40.5%, respectively. With regard to GWP, activated carbon and the direct emission during the combustion of HYO and natural gas are the main factors, accounting for 43.5 and 50.0%, respectively.

3.3.2. Environmental and Economic Performance.

3.3.2.1. Production Cost and Environmental Cost.

The production cost was calculated by eq 3, and the price of materials involved was accorded to the average market price in China. Based on the annual treatment capacity of 100 thousand tons of WTs, the total investment of the whole system is CNY 330 million, including CNY 30 million for CBp upgrading. The raw material cost mentioned in the production cost list includes the cost of WTs and all resources added in the system, such as hydrogen (23,000 CNY/t), natural gas (2.56 CNY/m^3),

activated carbon (3000 CNY/t), limestone (370 CNY/t), nitric acid (2043 CNY/t), and so forth. Since the TPO upgrading process is similar to crude oil refining, the cost of this part is estimated based on the crude oil refining cost. The refining scale of Case 1 is relatively small owing to its integration. Therefore, the influence of refining scale on the production cost needs to be considered. Using the scale index method based on the annual scale of 2 million tons, the cost of TPO refining is 834 CNY/t−WTs for the annual treatment capacity of 50 thousand tons, with the scale coefficient taken as 1.45. In contrast to Case 1, the TPO refining unit in Case 2 is completely independent, so that oil products can be concentrated for large-scale upgrading or mixed with crude oil. The annual treatment capacity can reach 400 thousand tons, and the scale coefficient can be reduced to 1.17, significantly reducing the upgrading cost, which reaches 675.4 CNY/t−WTs. The data of costs are shown in Table S5. The production cost of Case 1 is 3579.8 CNY/t−WTs and that of Case 2 is 3635.7 CNY/t−WTs. Although the construction cost of TPO refining in Case 2 is lower with the increasing treatment capacity, the raw material cost rises owing to the additional input of natural gas, resulting in a higher production cost than that of Case 1. Besides, the environmental costs of two basic schemes were calculated according to the abovementioned environmental tax of water, air and solid pollutants. It is obtained that the environmental cost of Case 1 is 224 CNY/t−WTs and that of Case 2 is 246.1 CNY/t−WTs.

3.3.2.2. Economic Benefit.

Since the qualities of gasoline and diesel are lower than that of the commercial oil products, their prices are below the market price, only 4000−6000 CNY/t and 3500−5000 CNY/t, respectively. Moreover, the prices of steel wire, heavy oil, M-CBp, steam, and low-quality steam are 1100−2200 CNY/t, 4000−4500 CNY/t, 4000−5000 CNY/t, 170−250 CNY/t, and 170−230 CNY/t, respectively. Combined with the yields of various products obtained from simulation, the economic benefits of Case 1 and Case 2 reach 3473.7 CNY/t−WTs and 3661.6 CNY/t−WTs, respectively, as shown in Table S6.

In accordance with the production cost and economic benefit, the BCRs of two cases are 0.97 and 1.01, respectively. Although
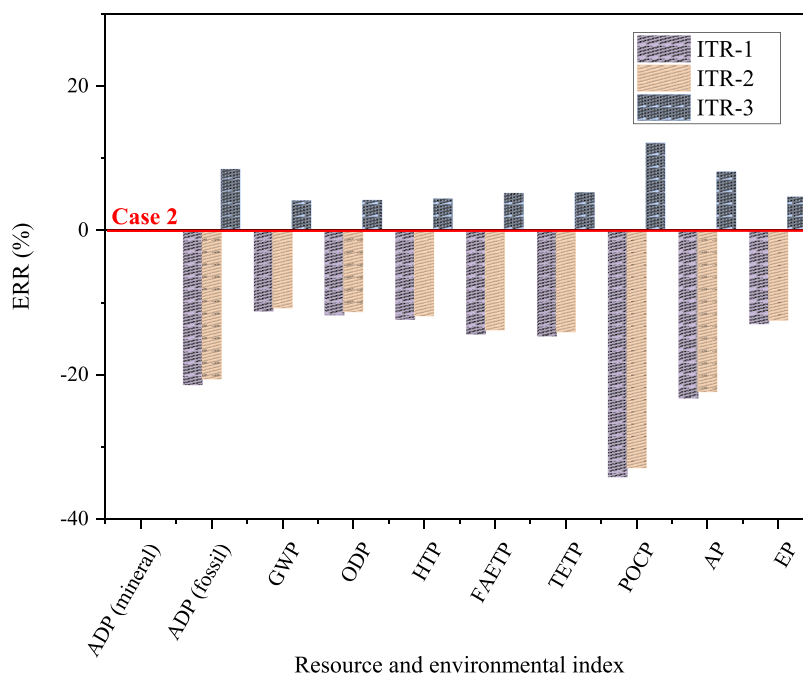
Figure 7. ERR of improved TPO refining paths.

the cost of Case 2 is higher than that of Case 1, the increase in the economic benefit exceeds the production cost due to the increase in the yields of the refined gasoline and steam. Therefore, the economic performance of Case 2 is better than that of Case 1.

Based on BCR, the BEECRs of Case 1 and Case 2 are evaluated to be 0.91 and 0.94, respectively. Obviously, the environmental-economic performances of the two cases are worse after integrating the environmental cost, especially Case 2 appears a deficit.

Based on the abovementioned environmental and economic analysis, by comparing our previous research results,[58] the production cost and environmental cost have increased. Furthermore, the profit of cases has also grown due to the improvement of product qualities. On the one hand, CBp is modified by nitric acid, which significantly increases the environmental load. On the other hand, the process of obtaining high-value products is so complex that the production cost increases. It indicates that the economic benefit increases through solid-phase and liquid-phase upgrading, but the comprehensive performance is not well improved. Therefore, the abovementioned cases need further optimization.

4. RESULTS AND DISCUSSION OF IMPROVED HIGH-VALUE PATHWAYS OF WT PYROLYSIS

4.1. Resource and Environmental Impacts. *4.1.1. Improved CBp Modification Paths.* To further improve the comprehensive performance of the basic high-value cases of WT pyrolysis, different improvement pathways were investigated for the CBp modification and TPO refining based on Case 2.

4.1.1.1. Chemical Modification. As mentioned in Section 3.3.1, obvious resource and environmental loads were generated by nitric acid in the chemical modification of CBp. To reduce the impact of this portion, the influence of nitric acid circulation number on resource consumption and environmental load was further explored. Figure 6 shows the ERR of doubling the circulation number. The ERR of ADP (mineral) reaches 49.6%,

and those of HTP and EP are more than 30%. Except for ADP (fossil) and POCP, the ERRs of other indicators are above 20%.

4.1.1.2. Physical Modification. It was obviously found that the largest resource and environmental impacts was caused in CBp modification according to Figure 5. To decrease the impact of the whole CBp upgrading process, physical modification was investigated. As shown in Figure 6, the ERR of ADP (mineral) is close to 100%, reaching 99.2%, followed by EP, HTP, and FAETP. Although the reduction rates of TETP, AP, and GWP are worse than the foregoing indexes, the value of ERR still exceeds 30%.

4.1.2. Improved TPO Refining (ITR) Paths. In terms of optimizing the quality of oil products to reach the national standard of China for refined oil (sulfur content ≤10 ppm), three possible improved approaches of TPO refining were proposed as shown below

1 Improved TPO refining path 1 (ITR-1): changing the sulfur distribution of pyrolysis products to reduce the sulfur content in TPO by adjusting the pyrolysis conditions and keeping the liquid-phase desulfurization efficiency unchanged. This improved path requires that at least 89.5% of sulfur in light pyrolysis oil and 64.8% of sulfur in medium pyrolysis oil are transferred into the vapor phase.

2 Improved TPO refining path 2 (ITR-2): increasing the gasoline hydrodesulfurization efficiency to 99% by further improvement in the catalytic effect. This improved path requires that at least 68.4% of sulfur in light pyrolysis oil and 64.8% of sulfur in medium pyrolysis oil are transferred into the vapor phase.

3 Improved TPO refining path 3 (ITR-3): adopting twice continuous HDS to make the quality of oil products meet the standard of sulfur content.

As shown in Figure 7, to a certain extent, ITR-1 and ITR-2 can reduce the resource and environmental impacts to achieve the purpose of emission reduction. ERR related with ITR-1 is slightly higher than that related with ITR-2. For three categories
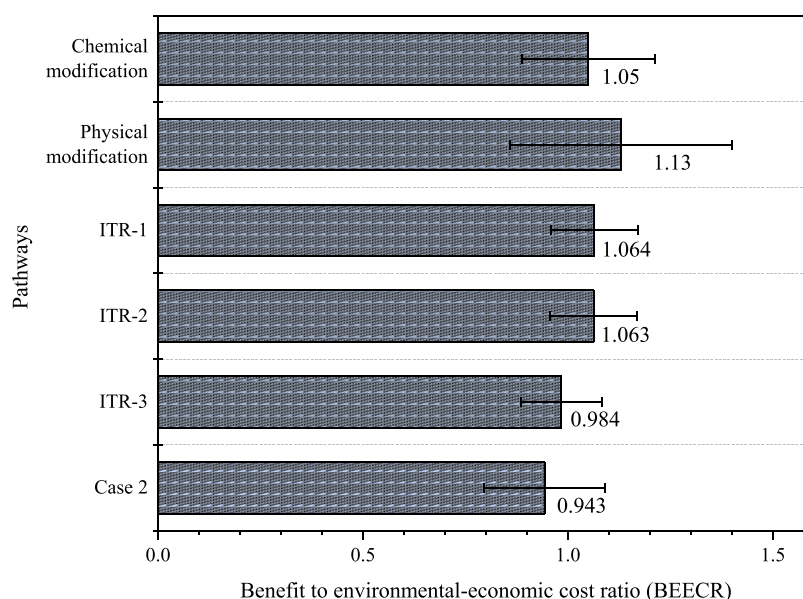
Figure 8. Comprehensive performance of improved high-value paths of WT pyrolysis.
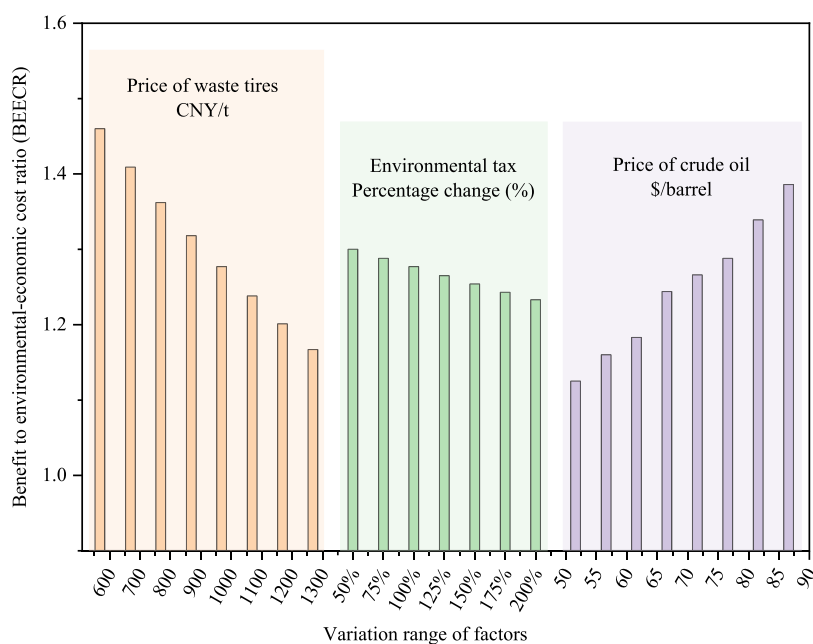

Figure 9. Sensitivity related with the comprehensive performance of the combined improved high-value path of CBp modification and TPO refining.

of indicators with the largest resource and environmental impacts mentioned above, the value of ADP (mineral) has barely changed in ITR-1 and ITR-2 because this load is almost caused by the CBp upgrading. As for HTP and FAETP, the ERR of these two indicators is between 10% and 20%. Due to the increase of the resource and energy input, the resource and environmental load of ITR-3 is higher than that of Case 2, so that there is no emission reduction benefit. The concrete resource and environmental impact data of improved TPO refining paths are listed in Table S7.

As mentioned above, it is better to adopt ITR-1 and ITR-2 from the perspective of resources and environment. Especially, it is beneficial to promote sulfur conversion during pyrolysis to reduce the sulfur content in TPO.

4.2. Comprehensive Performance. For improved TPO refining paths, the tax inclusive price of gasoline and diesel increased significantly, reaching 7600−8200 CNY/t and 6000−7000 CNY/t, respectively. The loss of M-CBp in physical modification significantly was reduced to 1%, and its price could reach half of the commercial carbon black, about 2500−5000 CNY/t. The cost of twice continuous HDS was estimated according to the proportion of the hydrodesulfurization unit in the total TPO upgrading cost, which was about 1.18 times that of basic cases. Considering the price fluctuation of products, the corresponding confidence interval was given for the value of BEECR.

It can be observed from Figure 8 that the comprehensive performances of abovementioned paths are improved compared with Case 2. Among them, the comprehensive performance of physical modification is the best, followed by ITR-1 and ITR-2. Chemical modification is relatively worse compared with abovementioned three improved paths, and the comprehensive

performance of ITR-3 is the weakest to no benefit owing to the high production cost.

4.3. Combined Improved High-Value Path of CBp Modification and TPO Refining. According to previous results, the combined improved high-value case was established based on the physical modification of CBp and ITR-1. The BEECR of the combined improved high-value path can increase to 1.28 when the WT cost is 1000 CNY/t (Figure 9), 13.3 and 20.3% growth compared with independent physical modification and ITR-1. Relative to the previous results of our study,[58] when the ratio of profit to environmental cost is used as the comprehensive evaluation index, the value of the index can achieve 8.81, significantly better than that of the original process (2.63).

Furthermore, the sensitivities of crude oil price, WT cost, and environmental tax were explored. The variation ranges of crude oil price and WT cost are 50−85 $/barrel and 600−1300 CNY/t, respectively, and that of the environmental tax is 100% up and 50% down. Results show that the environmental-economic cost is still dominated by the production cost. The share of environmental cost is so small that the tax fluctuation has little impact on the comprehensive performance of the system. Due to the good environmental performance of the combined improved high-value path, even if the environmental tax is doubled, the environmental performance remains well. The recycling price of WTs accounts for a large proportion of the production cost, and so, the fluctuation of the recycling price has a significant impact. Meanwhile, the rise of crude oil price directly touches off the soaring price of gasoline and diesel. When the ex-factory price of gasoline and diesel excluding tax reaches 8200 CNY/t and 7000 CNY/t (crude oil price is about 85 $/barrel), the value of BEECR can reach 1.39, and the net profit is significant. In addition, when the price of WTs rises to 1800 CNY/t and the ex-factory prices of gasoline and diesel fall to 3000 CNY/t and 2600 CNY/t, respectively, this path can still ensure positive economic benefits, implying that the allowable range of price changes in Figure 9 can be further expanded.

According to the result of sensitivity analysis, the SAs of the abovementioned three factors (crude oil price, WT cost, and environmental tax) were 53.7, 42.0, and 4.5%, respectively. BEECR is more sensitive to the prices of crude oil and WTs but less sensitive to the environmental tax, which means that the environmental load of the combined improved high-value path is small. To sum up, with the shortage of fossil resources and the rise in oil prices, WT pyrolysis to produce high-value products will bring significant environmental and economic benefits.

5. CONCLUSIONS

By the simulation and life cycle evaluation of WT pyrolysis and upgrading to obtain high-value products, the result shows that the comprehensive performance of independent system of TPO refining is better than that of the integrated system of pyrolysis, TPO refining, and CBp modification, with BEECR increasing by 3.3%.

Based on the independent system case (Case 2), two pathways, physical modification in solid phase upgrading and promoting sulfur conversion during pyrolysis (ITR-1) in liquid phase upgrading, demonstrate more significant advantages than other paths. The former makes the value of BEECR increase by 20.2% compared with Case 2, and the latter ensures that the growth of BEECR exceeds 13%.

If the abovementioned two methods are proposed together for scheme improvement, the comprehensive performance of combined improved high-value case will be optimal, which promotes the value of BEECR to be 1.28, with 13.3 and 20.3% growth compared with independent physical modification and ITR-1. Sensitivity analysis shows that the combined improved high-value case can achieve a great profit in a wide range of crude oil and WT prices and the environmental tax.

This study proposes and evaluates two basic WT pyrolysis cases to obtain high-value products combined with plant construction. Furthermore, improvement paths for the solid and liquid phases are proposed, respectively. Therefore, evaluation results of improved cases can provide a theoretical basis for subsequent process improvement. According to the current results, our subsequent research will focus on the closed loop of recycling pyrolytic products to produce new tires to achieve sustainable development. Moreover, new solid-phase modification methods to obtain the M-CBp with higher properties and better environmental-economic benefits will be further investigated to promote the broad application of WT pyrolysis. Meanwhile, it is necessary to further develop high-quality desulfurization catalysts to improve the quality of oil products so as to meet the requirements of refined oil.

■ ASSOCIATED CONTENT

ⓈI Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c02952.

> Component yield of non-condensable gas; group composition of gasoline fraction obtained from the experiment; group composition of diesel fraction obtained from the experiment; modeling component yield of TPO; production costs of Case 1 and Case 2; economic benefits of Case 1 and Case 2; and normalization of environmental impact of improved TPO refining paths (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

ABBREVIATIONS

WT   waste tire
TPO   tire pyrolytic oil
CBp   pyrolytic carbon black
HDS   hydrodesulfurization
DBT   dibenzothiophene
M-CBp   modified carbon black
LCA   life cycle assessment
HYO   heavy oil
ADP   abiotic depletion potential
GWP   global warming potential
ODP   ozone layer depletion potential
HTP   human toxicity potential
FAETP   freshwater aquatic eco-toxicity potential
TETP   terrestrial eco-toxicity potential
POCP   photochemical oxidation potential
AP   acidification potential
EP   eutrophication potential
ITR   improved TPO refining

VARIABLES

ERE   energy recovery efficiency
EUE   effective utilization energy
TIE   total input energy
ERR   emission reduction rate
SV   standardized value
BCR   benefit to cost ratio
P_j price of product j
M_j mass of product j
C^p production cost
BEECR   benefit to environmental-economic cost ratio
C^e environmental cost
SA_x sensitivity

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