# Comparative Life Cycle Assessment of Co-Processing of Bio-Oil and Vacuum Gas Oil in an Existing Refinery

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Keywords: co-processing, bio-oil, vacuum gas oil, LCA, Eco-indicator 99, FCC

#### Abstract:

The co-cracking of vacuum gas oil (VGO) and bio-oil has been proposed to add renewable carbon into the co-processing products. However, the environmental performance of the co-processing scheme is still unclear. In this paper, the environmental impacts of the co-processing scheme are calculated by the end-point method Eco-indicator 99 based on the data from actual industrial operations and reports. Three scenarios, namely fast pyrolysis scenario, catalytic pyrolysis scenario and pure VGO scenario, for two cases with different FCC capacities and bio-oil co-processing ratios are proposed to present a comprehensive comparison on the environmental impacts of the co-processing scheme. In Case 1, the total environmental impact for the fast pyrolysis scenario is 1.14% less than that for the catalytic pyrolysis scenario while it is only 26.1% of the total impacts of the pure VGO scenario. In Case 2, the environmental impact of the fast pyrolysis scenario is 0.07% more than that of the catalytic pyrolysis and only 64.4% of the pure VGO scenario impacts. Therefore, the environmental impacts can be dramatically reduced by adding bio-oil as the FCC co-feed oil, and the optimal bio-oil production technology is strongly affected by FCC capacity and bio-oil co-processing ratio.

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**Abstract**: The co-cracking of vacuum gas oil (VGO) and bio-oil has been proposed to add renewable carbon into the co-processing products. However, the environmental performance of the co-processing scheme is still unclear. In this paper, the environmental impacts of the co-processing scheme are calculated by the end-point method Eco-indicator 99 based on the data from actual industrial operations and reports. Three scenarios, namely fast pyrolysis scenario, catalytic pyrolysis scenario and pure VGO scenario, for two cases with different FCC capacities and bio-oil co-processing ratios are proposed to present a comprehensive comparison on the environmental impacts of the co-processing scheme. In Case 1, the total environmental impact for the fast pyrolysis scenario is 1.14% less than that for the catalytic pyrolysis scenario while it is only 26.1% of the total impacts of the pure VGO scenario. In Case 2, the environmental impact of the fast pyrolysis scenario is 0.07% more than that of the catalytic pyrolysis and only 64.4% of the pure VGO scenario impacts. Therefore, the environmental impacts can be dramatically reduced by adding bio-oil as the FCC co-feed oil, and the optimal bio-oil production technology is strongly affected by FCC capacity and bio-oil co-processing ratio.

Keywords: co-processing; bio-oil; vacuum gas oil; LCA; Eco-indicator 99; FCC

# 1. Introduction

To ensure the sustainable development of society, developing renewable fuels with less CO<sub>2</sub> emission is of vital significance considering the lack of fossil resources and the greenhouse effect [1]. Developing bio-fuels can serve for solving the resource shortage issue as well as easing environmental burden [2]. Furthermore, as crude oil becomes sourer and heavier, and demand for high-grade gasoline and diesel keeps increasing, developing the renewable energy of bio-fuels with a lower sulfur impurity has drawn people's attention [3].

Bio-diesel and bio-gasoline have much higher prices compared to diesel and gasoline derived from petroleum, because the biomass is much more expensive than crude oil and a bio-refinery needs a large capital investment [4]. In addition, bio-diesel and bio-gasoline only contain part of distillates of diesel and gasoline derived from petroleum, thus a further blending process is needed. Thus, currently, the research hotspot lies in the way to remarkably lower the production cost of the two kinds of bio-fuels while satisfying the national standards regarding bio-fuels [5,6].

Bio-oil and vacuum gas oil (VGO) co-processing in an existing fluid catalytic cracker (FCC) to produce gasoline and diesel with renewable carbon has been proposed to lower the production cost of bio-fuels by using the existing infrastructures of a refinery [7,8].

According to the previous studies [9,10], the bio-oils obtained from catalytic pyrolysis and fast pyrolysis can both be co-processed with VGO. Graca et al. [11] used several key model compounds to represent the bio-oil and then co-fed the bio-oil with VGO into an FCC to obtain gasoline and diesel. They showed that up to 10% of model compounds



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**Copyright:** © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). can be co-processed with VGO and no severe problems are generated in the FCC. In the study by Pinho et al. [12,13], 10% fast pyrolysis bio-oil was directly co-fed with VGO and adding renewable carbon in gasoline and diesel did not largely affect the production yield. A remarkable increase of coke yield would be observed if more bio-oil were co-processed. As the fast pyrolysis oil exhibits a high content of oxygen and a low enthalpy, the hydrodeoxygenation (HDO) of the bio-oil and subsequent VGO co-processing were proposed [14]. Compared to the pure VGO cracking, the similar gasoline and diesel yields were obtained when the HDO oil was used as the co-feedstock. Up to 10% HDO oil can be co-fed with VGO in an FCC for maintaining the yields of gasoline and diesel as well as the coke yield [15].

Regarding the co-processing of catalytic pyrolysis oil and the VGO, Wang et al. [16] revealed that up to 10% catalytic pyrolysis oil could be co-processed with VGO directly without affecting the gasoline yield. More than 7% bio-carbon can be detected in the co-processing gasoline via <sup>14</sup>C analysis. Lindfors et al. investigated three types of bio-oil: fast pyrolysis oil, catalytic pyrolysis oil and HDO oil [17]. The results show that the coke yield would increase if more than 20% bio-oil were co-fed with VGO. Compared to gasoline yields for the co-processing of catalytic pyrolysis oil or HDO oil, the yields for the co-processing of fast pyrolysis oil were the lowest due to its high oxygen content. Similar gasoline yields were obtained if the HDO oil or the catalytic pyrolysis oil was used as the co-feedstock with VGO. Hence, it is possible to co-feed catalytic pyrolysis oil directly with VGO if its co-processing ratio is less than 10% [18].

As both the HDO oil and the catalytic pyrolysis oil can co-process with VGO in an FCC, the top priority should lie in selecting the optimal production process of bio-oil. Wu et al. proposed a superstructure model [19] and a techno-economic analysis [20], where the total annual cost and the gasoline selling price is minimized to select the best biomass feedstock and the most suitable production process of bio-oil. The results show that the most suitable production process of bio-oil exhibits a strong dependence on the bio-oil co-processing ratio and the capability exhibited by the co-processing FCC.

Researchers have considered the feasibility [21], kinetics [22], modeling [23], optimization [24] and economics [25] of bio-oil and VGO co-processing for decades, but the co-processing research is still active due to its complexity [26]. As the key advantage of the co-processing technique is to lower the environmental pollution by adding renewable energy to a fossil fuel refinery [27], the environmental impacts of the co-processing process also attract attention [28]. Life cycle assessment (LCA) enjoys a wide application in the evaluation of the environmental impacts of chemical processes [29,30], especially for bio-processes [31]. Cruz et al. [32] used the LCA software SimaPro 8.5 to analyze the environmental performance of four cases based on the data of Aspen Plus simulations. This study gives the basic framework for the assessment of co-processing process.

Based on Cruz et al.'s study [28,32], an endpoint method based on LCA, Eco-indicator 99 [33], assists in quantifying the environmental impacts of the co-processing schemes integrating fast pyrolysis or catalytic pyrolysis as the bio-oil source. Aiming to understand the environmental impacts of the co-processing scheme, a LCA was conducted to obtain the optimal bio-oil production process from fast pyrolysis and catalytic pyrolysis with minimized environmental impacts. The study also investigated the way that the FCC capability and bio-oil co-processing ratio affect the environmental impacts together with the optimal production process of bio-oil.

#### 2. Materials and Methods

#### 2.1. Co-Processing Scheme

Figure 1 displays the co-processing, which contains the bio-oil production process and the co-processing process in an existing refinery.



Figure 1. Process flowsheet of bio-oil co-processing with VGO.

With regard to the bio-oil production process, catalytic pyrolysis or fast pyrolysis is adopted to crack the biomass feedstock as well as produce bio-oil. As for the fast pyrolysis oil, the content of oxygen is high and the enthalpy value is low, making it necessary to perform a further hydrotreatment for removing the extra oxygen impurities as well as obtaining the HDO oil in a hydrotreating (HDT) process.

Regarding the bio-oil and VGO co-processing in the existing refinery, the upgraded bio-oil, co-feeding HDO oil or catalytic pyrolysis oil with VGO into the FCC helps to generate the gasoline and diesel, followed by the upgrading in relevant HDT processes. The upgraded diesel and gasoline with renewable carbon are finally produced. The reactor type of the pyrolysis process is the circulating fluidized bed which is the same reactor used in a US Department of Energy report [34].

As pulpwood is a common biomass and its economic advantage in the co-processing with VGO has been shown [20], it was chosen as the feedstock. A refinery located in Ningbo, China was used as the co-processing refinery. According to the relevant studies [20], our previous studies [20,35] and the average data from monthly technical reports, the basic properties and main operating parameters of the above-mentioned processes are listed in Tables 1 and 2. The operating conditions of fast pyrolysis, catalytic pyrolysis and FP oil HDT were obtained from the literature, while the operating conditions of the FCC, diesel HDT and gasoline HDT were derived from actual industrial operations.

Process		Refined VGO	HDO Oil [34]	Catalytic Pyrolysis Oil [36]
Density/kg·m <sup>-3</sup>		915.5	848	1010
	IBP	308	/	151
	10%	399	59	172
Distillation curve <sup>1</sup> /°C	30%	491	101	243
	50%	552	170	300
	70%	608	231	352
	90%	673	346	466
	FBP	700	405	629

Table 1. Basic properties of refined VGO, HDO oil and catalytic pyrolysis oil.

<sup>1</sup> Distillation curves of refined VGO, HDO oil and catalytic pyrolysis oil are tested by ASTM D86, ASTM D2887 and ASTM D4052, respectively.

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Table 7	Inorating	narametere	of the co-	nrocessing	chomo
1abic 2.	Operating	parameters	or the co	processing a	scheme.

Process	Temperature/°C	Pressure/Bar	H <sub>2</sub> /Oil Ratio	References
Fast pyrolysis	500	1.013	/	[34]
Catalytic pyrolysis	500	1.013	/	[5]
FP oil HDT	180/350 <sup>1</sup>	137.89	12.9	[34]
FCC	495	1.4	/	[35]
Diesel HDT	313	70.5	300	[35]
Gasoline HDT	258	21	200	[35]

<sup>1</sup> Temperatures of the first and second stages in a two-stage HDT reactor.

#### 2.2. Life Cycle Assessment

LCA boosts a wide application in the evaluation of the environmental impacts caused by a chemical process. The total environmental impacts of the co-processing scheme are calculated by the endpoint method of Eco-indicator 99 followed by ISO 14040 2006 [37].

# 1. Goal and scope definition

The study's primary goal was identifying the environmental impacts of the coprocessing scheme, as well as selecting the optimal bio-oil production technology because fast pyrolysis and catalytic pyrolysis can both serve for producing upgraded bio-oil for the co-processing with VGO.

The whole co-processing scheme is set as the system boundary shown in Figure 2, which contains the bio-oil production process involving the fast pyrolysis and the following HDT process or catalytic pyrolysis, bio-oil and VGO co-processing in FCC and gasoline and diesel HDT processes. The functional unit is the total environmental impacts of all the input and output streams using an end-point evaluation method. As the main purpose of this study was to quantify the environmental impacts of the production phase of the co-processing scheme, the phases of individual units commissioning and shutdown were ignored in the analysis.



Figure 2. System boundary of the co-processing scheme.

#### 2. Inventory analysis

According to Figure 2, the input of the co-processing scheme is mainly the raw materials, hydrogen and utilities, while the output is the gas products, gasoline and diesel. It should be pointed out that only 5% slurry oil from the bottom of the FCC is usually used as a recycled oil to increase the gasoline yield. The consumptions of raw materials, water, hydrogen and products can be calculated considering the mass balance of the co-processing scheme. The electricity and steam consumptions can be derived from the energy balance. The equations for the mass balance and energy balance are presented in the Supplementary Materials.

# 3. Impact assessment

In this step, the total environmental impacts of the co-processing scheme were calculated according to the consumptions of raw materials, utilities and products multiplied by their damage factors, as shown in Equation (4).

Damage factor, the possible damage to the environment due to an emission or consumption of a material listed in life cycle inventory of Eco-invent, can be calculated by Equations (1)–(3) according to the methodology of Eco-indicator 99 [33]. The life cycle impact factor of a material can be obtained from the data of Eco-indicator in Eco-invent [37].

$$DF_{rm} = \sum_{c,rm} LCIF_{c,rm} \tag{1}$$

$$DF_u = \sum_c LCIF_{c,u} \tag{2}$$

$$DF_p = \sum_c LCIF_{c,p} \tag{3}$$

where DF is the damage factor, in pt per unit raw materials, utilities and products. LCIF denotes the life cycle impact factor. Subscripts rm, u and p are the sets for raw materials, utilities and products, respectively. Subscript c is the ten impact categories in the Eco-indicator 99, namely acidification and eutrophication, land occupation, ecotoxicity, carcinogens, climate change, ionizing radiation, ozone layer depletion, respiratory effects, fossil fuels and mineral extraction.

$$TEI = (EI_{\rm RM} + EI_{\rm U} + EI_{\rm P})t \tag{4}$$

$$EI_{\rm RM} = \sum_{rm} m_{rm} DF_{rm} \tag{5}$$

$$EI_{\rm U} = \sum_{u} m_u DF_u \tag{6}$$

$$EI_{\rm P} = \sum_{p} m_p DF_p \tag{7}$$

where *TEI* is the total environmental impacts, in  $pt \cdot y^{-1}$ ; *t* denotes the annual operating time, in  $h \cdot y^{-1}$ ; *m* represents the material and utility consumption, as well as the production of products; and subscripts RM, U and P are raw materials, utilities and products, respectively.

#### 3. Results and Discussion

The co-processing scenarios of fast pyrolysis and catalytic pyrolysis are proposed based on the two productive processes: the integrated fast pyrolysis (HDO) and the catalytic pyrolysis. Moreover, the existing operating scenario of the refinery, pure VGO scenario, is also adopted to give a direct comparison with the two co-processing scenarios. Two cases are also proposed to illustrate the effects of the bio-oil co-processing ratio and the annual capability exhibited by the co-processing FCC on the environmental impacts brought about by the co-processing scheme. The key parameters of the two cases are shown in Table 3. Tables 4 and 5 list the damage factors regarding input streams of raw materials

and utilities and output streams of: products. The process yields and impurity contents of HDT processes are presented in Tables 6 and 7.

Table 3. Key parameters of Cases 1 and 2.

	Case 1	Case 2
FCC capability/t·y <sup>-1</sup>	1,200,000	600,000
Bio-oil co-processing ratio/%	10	5

Table 4. Damage factors of input streams: raw materials and utilities.

Items	Pulpwood <sup>1</sup> /pt·m <sup>-3</sup>	VGO/pt ·t <sup>−1</sup>	$H_2/pt \cdot t^{-1}$	Water/pt ·t <sup>-1</sup>	Steam/pt ·t <sup>-1</sup>	Electricity/pt·kWh <sup>-1</sup>
Damage factor	2.1388	182.57	246.71	0.050054	1.94	0.06486
	1				2	

 $^1$  The pulpwood density after air dried is assumed as 0.85 t  $\cdot m^{-3}.$ 

Table 5. Damage factors of output streams: products.

Items	Gasoline/pt ⋅t <sup>-1</sup>	Diesel/pt ⋅t <sup>-1</sup>	Slurry Oil/pt t <sup>-1</sup>	Bio-Gas/pt ⋅t <sup>-1</sup>	Fuel Gas/pt ≀t <sup>-1</sup>	Co-Processing Gas/pt·t <sup>-1</sup>
Damage factor	183.369	192.01	285.61	12.504	189.55	189.26

Table 6. Product yields of all the related processes.

Process	Product	Yield/%	References
	Bio-oil	52.5	
Fast pyrolysis	Bio-gas	26.0	[38]
	Bio-char	21.5	
	Bio-oil	33.0	
Catalytic pyrolysis	Bio-gas	53.0	[38]
	Bio-char	12.5	
	Fuel gas	1.4	
Fast pyrolysis oil HDT	HDO oil	66.0	[38]
	Aqueous phase	34.6	
	Co-processing gas	18.0	
ECC	FCC gasoline	48.1	[5]
FCC	FCC diesel	23.0	
	Slurry oil	5.9	
ECC gasalina HDT	Fuel gas	0.5	[=]
FCC gasoline HD1	Gasoline	99.5	[0]
	Fuel gas	1.2	
FCC diesel HDT	Gasoline	7.63	[5]
	Diesel	91.2	-

Table 7. Impurity contents of inlet and outlet streams in HDT processes [19].

Process		Sulfur/ppm	Nitrogen/ppm	Aromatics/%	Oxygen/ppm
Fast pyrolysis oil HDT	Inlet Outlet	0 0	9800 5000	/ /	450,000 250,000
FCC gasoline HDT	Inlet	161	42	20.7	434
	Outlet	10	10	20	50
FCC diesel HDT	Inlet	1948	336	48.8	365
	Outlet	50	15	35	50

# 3.1. Case 1

3.1.1. Material Balance and Energy Balance

Ten percent bio-oil is co-processed with 90% VGO in an FCC and the processing capability reaches  $1.2 \times 10^6$  t·y<sup>-1</sup>. The mass balance as well as the energy balance are calculated according to the equations in the Supplementary Materials, which are shown in Figure 3.



Figure 3. Main mass and energy balances of the three scenarios in Case 1.

According to Figure 3, the main differences between the two co-processing scenarios lie in the production process of bio-oil as well as the hydrogen consumption in the existing gasoline and diesel HDT units. In the fast pyrolysis scenario,  $41.23 \text{ t}\cdot\text{h}^{-1}$  biomass is pyrolyzed in the reactor and then  $14.29 \text{ t}\cdot\text{h}^{-1}$  bio-oil is obtained to be co-processed with 128.57 t $\cdot\text{h}^{-1}$  VGO. In total,  $5.3 \text{ t}\cdot\text{h}^{-1}$  steam and 8570.24 kW electricity are consumed in the pyrolysis and HDT processes. In the catalytic pyrolysis scenario,  $14.29 \text{ t}\cdot\text{h}^{-1}$  bio-oil is produced with the consumption of  $43.29 \text{ t}\cdot\text{h}^{-1}$  biomass in the catalytic pyrolysis reactor. In total,  $12.47 \text{ t}\cdot\text{h}^{-1}$  steam and 8866.67 kW electricity are consumed in the catalytic pyrolysis. The reason for the difference of hydrogen consumption of gasoline and diesel HDT processes in the two scenarios is the different oxygen contents of the HDO oil and catalytic pyrolysis oil.

The differences between the two co-processing scenarios and the pure VGO scenario are the flowrate of the refined VGO and the hydrogen consumptions of the diesel and gasoline HDT processes. The consumptions of electricity and steam in the pure VGO scenario are the same as the relevant processes in the two co-processing scenarios because these consumptions are assumed unchanged due to the relatively small amount of the bio-oil compared to the VGO amount.

The total consumptions of raw materials and utilities as well as the products are listed in Table 8.

	Items		Fast Pyrolysis	Catalytic Pyrolysis	Pure VGO
	D ( ) 1	Biomass/t·year <sup>-1</sup>	346,332.00	363,636	0
	Raw materials	VGO/t·year <sup>-1</sup>	1,079,988.00	1,079,988.00	1,200,024
Innut streams		$H_2/t$ ·year <sup>-1</sup>	7140.00	5224.80	4930.80
niput streams	TI::::	Water/t·year <sup>-1</sup>	211,693.50	193,150.40	100,000
	Utilities	Steam/t∙year <sup>-1</sup>	256,536.00	316,764.00	212,016
		$Electricity/kWh \cdot year^{-1}$	106,740,816	109,230,828.00	34,750,800
		Gasoline/t·year <sup>-1</sup>	595,392.00	595,392.00	595,392.00
	Products	Diesel/t·year <sup>−1</sup>	251,748.00	251,748.00	251,748.00
0 1 1 1		Slurry oil/t·year <sup><math>-1</math></sup>	67,284.00	67,284.00	67,284.00
Output streams		Bio-gas/t·year <sup><math>-1</math></sup>	17,976.00	38,556.00	0
		Fuel gas/t·year <sup>-1</sup>	8744.40	6199.20	222,163.20
		Co-processing $gas/t$ ·year <sup>-1</sup>	215,964.00	215,964.00	0

Table 8. Total consumptions of raw materials and utilities as well as products in Case 1.

#### 3.1.2. LCA Results

As displayed in Figure 3 and Tables 4, 5 and 8, the methodology of Eco-indicator 99 was used to calculate the environmental impacts of the three scenarios, which are shown in Figure 4.



Figure 4. Environmental impacts of the three scenarios in Case 1.

According to Figure 4, the environmental impact of VGO is  $1.97 \times 10^8$  pt·year<sup>-1</sup>, which is the largest among all the impacts for the fast pyrolysis scenario as well as the catalytic pyrolysis scenario. The VGO impact in the pure VGO scenario reaches  $2.19 \times 10^8$  pt·year<sup>-1</sup>. The largest VGO proportion is caused by the large consumption of VGO and its higher damage factor. The results are in accordance with those of Cruz et al. [32]. Due to the relatively lower consumptions compared to VGO, the impacts of biomass and utilities can be ignored, especially for the impacts of water and steam. The second large proportions of the three scenarios are the electricity impacts of  $6.92 \times 10^6$ ,  $7.08 \times 10^6$  and  $2.25 \times 10^6$  pt·year<sup>-1</sup>, respectively. As for the contributions of products, gasoline shows the largest contribution to environment with  $1.14 \times 10^8$  pt·year<sup>-1</sup> while the bio-gas has the smallest one at  $2.25 \times 10^5$  pt·year<sup>-1</sup> for the fast pyrolysis scenario and  $4.82 \times 10^5$  pt·year<sup>-1</sup> for the catalytic pyrolysis scenario. The total environmental impact of the fast pyrolysis scenario is  $5.83 \times 10^6$  pt·year<sup>-1</sup> and that of the catalytic pyrolysis scenario is  $5.90 \times 10^6$  pt·year<sup>-1</sup>, while the impact of the pure VGO scenario is  $2.23 \times 10^7$  pt·year<sup>-1</sup>, which is only 26.1% of the impacts of the co-processing scenarios. Therefore, the co-processing technique is an environmental impacts of the existing refinery infrastructures can be dramatically reduced by co-cracking with bio-oil. This conclusion is consistent with the GWP results of Cruz et al. [32]. According to the comparisons of the two co-processing scenarios, the optimal bio-oil production technology is fast pyrolysis.

#### 3.2. Case 2

#### 3.2.1. Material Balance and Energy Balance

In Case 2, 5% bio-oil is co-processed with 95% VGO in an FCC and the processing capability reaches  $6 \times 10^5$  t·year<sup>-1</sup>. The mass and energy balances are shown in Figure 5.



Figure 5. Main mass and energy balances of the three scenarios in Case 2.

Similar to the mass and energy balances of Case 1 shown in Figure 4, the main differences between the two co-processing scenarios in Case 2 lie in the production process of bio-oil and the hydrogen consumption in existing gasoline and diesel HDT unit. Overall,  $10.31 \text{ t} \cdot \text{h}^{-1}$  biomass is pyrolyzed and then hydrotreated to produce  $3.57 \text{ t} \cdot \text{h}^{-1}$  HDO oil. The obtained HDO oil is then co-fed with  $67.86 \text{ t} \cdot \text{h}^{-1}$  VGO into FCC for obtaining gasoline and diesel of 34.36 and  $16.43 \text{ t} \cdot \text{h}^{-1}$ , respectively, which are then hydrotreated in the relevant HDT processes. The total steam consumption and electricity consumptions are  $13.96 \text{ t} \cdot \text{h}^{-1}$  and 4210.91 kW in the fast pyrolysis scenario, respectively. In the catalytic pyrolysis scenario,  $10.81 \text{ t} \cdot \text{h}^{-1}$  biomass is consumed to produce  $3.57 \text{ t} \cdot \text{h}^{-1}$  bio-oil for the co-processing with VGO. In total,  $15.75 \text{ t} \cdot \text{h}^{-1}$  steam and 4285.31 kW electricity are consumed in the catalytic pyrolysis.

As for the comparisons between the two co-processing scenarios and the pure VGO scenario, the main difference of the existing FCC and HDT processes is the hydrogen consumption as there is no need to remove the oxygen impurities in bio-oil.

#### 3.2.2. LCA Results

The environmental impacts of the three scenarios in Case 2 were calculated according to the data in Tables 4, 5 and 9 and Figure 5.

		1		1	
	Items		Fast Pyrolysis	Catalytic Pyrolysis	Pure VGO
	Description to at a la	Biomass∕t·year <sup>−1</sup>	86,604.00	90,888	0
	Kaw materials	VGO/t·year <sup>-1</sup>	570,024.00	570,024.00	600,012
Innut streams		$H_2/t$ ·year <sup>-1</sup>	4376.40	3805.20	3729.60
input sticulis	TICLE	Water/t·year <sup>−1</sup>	63,636.37	59,000.00	50,000
	Utilities	Steam/t·year <sup>-1</sup>	117,012.00	132,300.00	106,092
		Electricity/kWh∙year <sup>-1</sup>	35,371,644	35,996,604.00	17,375,484
		Gasoline/t∙year <sup>-1</sup>	297,696.00	297,696.00	297,696.00
		Diesel/t∙year <sup>-1</sup>	125,832.00	125,832.00	125,832.00
		Slurry oil/t·year <sup><math>-1</math></sup>	33,600.00	33,600.00	33,600.00
Output streams	Products	Bio-gas/t·year <sup><math>-1</math></sup>	4536.00	9660.00	0
		Fuel gas/t·year <sup>-1</sup>	3738.00	3099.60	111,123.60
		Co-processing gas/t·year <sup>-1</sup>	108,024.00	108,024.00	0

Table 9. Total consumptions of raw materials and utilities as well as the products in Case 2.

According to Figure 6, the environmental impact of VGO is  $1.04 \times 10^8$  pt·year<sup>-1</sup> and the VGO impact is the largest proportion among all the impacts for the fast pyrolysis scenario as well as the catalytic pyrolysis scenario with only 5% bio-oil co-processed with 95% VGO, while the VGO impact in the pure VGO scenario is as large as  $1.1 \times 10^8$  pt·year<sup>-1</sup>. Similar to Case 1, the impacts of biomass and utilities can be ignored compared the large VGO impacts. The second largest contribution of the two co-processing scenarios is the electricity impact of  $2.29 \times 10^6$  and  $2.33 \times 10^6$  pt·year<sup>-1</sup> while the electricity impact in the pure VGO scenario is  $1.13 \times 10^6$  pt·year<sup>-1</sup>. As for the contributions of products, gasoline shows the largest contribution with  $5.46 \times 10^7$  pt·year<sup>-1</sup> while the bio-gas has the smallest contribution with  $5.67 \times 10^4$ ,  $1.21 \times 10^5$  and 0 pt·year<sup>-1</sup> for the three scenarios, respectively. The total environmental impact of the fast pyrolysis scenario is 0.07% higher than that of the catalytic pyrolysis. The reduction of the total environmental impacts of the existing FCC and HDT processes can reach 73.6% with only 5% catalytic pyrolysis bio-oil added in the FCC feed.



Figure 6. Environmental impacts of the three scenarios in Case 2.

# 3.3. Effects of FCC Feed Density and Temperature on Environmental Impacts3.3.1. Effect of FCC Feed Density

The effect of the FCC feed density on the environmental impacts is obtained according to the actual operating data of FCC, which is shown in Figure 7. The yields of all products of the FCC are listed in the Supplementary Materials.



Figure 7. Effect of FCC feed density on environmental impacts.

According to Figure 7, the environmental impacts of all the three scenarios are increased with the increase of FCC feed oil density. Similar to the results of Case 1, the fast pyrolysis scenario has the minimum environmental impact compared with the other scenarios, which is only 20% of the impacts of pure VGO scenario. Therefore, the lighter feed oil of FCC can reduce the environmental impacts.

## 3.3.2. Effect of FCC Operating Temperature

The effect of the FCC feed density on the environmental impacts was obtained according to the actual operating data of FCC, which is shown in Figure 8. The yields of all products of the FCC are listed in the Supplementary Materials.



Figure 8. Effect of FCC operating temperature on environmental impacts.

According to Figure 8, the environmental impacts of all the three scenarios are reduced with the increase of FCC operating temperature. The fast pyrolysis scenario has the minimum environmental impact compared with the other scenarios, which is only 10% of the impacts of pure VGO scenario. The main reason for this is that more light products like fuel gas, gasoline are produced, which have a relative lower damage factors.

#### 4. Conclusions

The co-processing of bio-oil and VGO has been proposed to lower the production cost of bio-fuels with the infrastructures of an existing refinery. In this study, Eco-indicator 99 was adopted to evaluate the environmental impacts imposed by the co-processing scheme including the bio-oil production process and the co-processing of bio-oil and VGO.

Two cases were proposed to investigate the way bio-oil co-processing ratio and the capability of co-processing FCC affect the total environmental impacts of the co-processing scheme. Moreover, three scenarios, namely fast pyrolysis, catalytic pyrolysis and pure VGO scenarios, were put forward to compare their environmental impacts. In Case 1, the results show that the fast pyrolysis scenario and the catalytic pyrolysis scenario generate total environmental impacts of  $4.21 \times 10^7$  and  $4.26 \times 10^7$  pt·year<sup>-1</sup>, respectively, while the impact of the pure VGO scenario is  $5.87 \times 10^7$  pt·year<sup>-1</sup>. The optimal bio-oil production technology for Case 1 is fast pyrolysis. In Case 2, the environmental impact of the fast pyrolysis scenario is 0.07% more than those of the catalytic pyrolysis and only 64.4% of the pure VGO scenario impacts. Thus, catalytic pyrolysis should be chosen for the bio-oil production in Case 2. Therefore, the environmental impacts of the existing infrastructures can be dramatically reduced by adding the bio-oil as the FCC co-feed oil. The optimal bio-oil production technology is determined by the FCC capacity and bio-oil co-processing ratio. Furthermore, the environmental impacts of VGO are the largest proportion of the total impacts, which means that the non-renewable raw material still takes the largest contribution of all the environmental impacts. Decreasing the VGO consumption or increasing the bio-oil/VGO feed ratio can most effectively lower the environmental impacts brought about by the co-processing scheme.

The environmental impacts of the co-processing scheme should be considered when designing the scheme. As the impacts of the non-renewable feedstock are the largest impacts of the scheme, the future direction of the co-processing technique may be to increase the bio-oil quality, thus more bio-oil can be added into the FCC without decreasing the gasoline yield.

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## References

- 1. Mohammadi, A.; Khoshnevisan, B.; Venkatesh, G.; Eskandari, S. A Critical Review on Advancement and Challenges of Biochar Application in Paddy Fields: Environmental and Life Cycle Cost Analysis. *Processes* **2020**, *8*, 1275. [CrossRef]
- Chen, S.; Feng, H.; Zheng, J.; Ye, J.; Song, Y.; Yang, H.; Zhou, M. Life Cycle Assessment and Economic Analysis of Biomass Energy Technology in China: A Brief Review. *Processes* 2020, *8*, 1112. [CrossRef]
- 3. Filippa, F.; Panara, F.; Leonardi, D.; Arcioni, L.; Calderini, O. Life Cycle Assessment Analysis of Alfalfa and Corn for Biogas Production in a Farm Case Study. *Processes* 2020, *8*, 1285. [CrossRef]
- 4. Cruz, N.C.; Silva, F.C.; Tarelho, L.A.C.; Rodrigues, S.M. Critical review of key variables affecting potential recycling applications of ash produced at large-scale biomass combustion plants. *Resour. Conserv. Recycl.* **2019**, *150*, 104427. [CrossRef]
- 5. Vasalos, I.A.; Lappas, A.A.; Kopalidou, E.P.; Kalogiannis, K.G. Biomass catalytic pyrolysis: Process design and economic analysis. *Wiley Interdiscip. Rev. Energy Environ.* **2016**, *5*, 370–383. [CrossRef]
- 6. Kan, T.; Strezov, V.; Evans, T.J. Lignocellulosic biomass pyrolysis: A review of product properties and effects of pyrolysis parameters. *Renew. Sustain. Energy Rev.* **2016**, *57*, 1126–1140. [CrossRef]
- Stefanidis, S.D.; Kalogiannis, K.G.; Lappas, A.A. Co-processing bio-oil in the refinery for drop-in biofuels via fluid catalytic cracking. Wiley Interdiscip. Rev. Energy Environ. 2018, 7, e281. [CrossRef]
- 8. Wu, L.; Wang, J.; Wang, Y.; Zheng, L. Design and Integration of Bio-Oil Co-Processing with Vacuum Gas Oil in a Refinery. *Chem. Eng. Trans.* **2019**, *76*, 1171–1176.
- 9. Graça, I.; Ribeiro, F.R.; Cerqueira, H.S.; Lam, Y.L.; de Almeida, M.B.B. Catalytic cracking of mixtures of model bio-oil compounds and gasoil. *Appl. Catal. B Environ.* 2009, 90, 556–563. [CrossRef]
- 10. Fogassy, G.; Thegarid, N.; Toussaint, G.; van Veen, A.C.; Schuurman, Y.; Mirodatos, C. Biomass derived feedstock co-processing with vacuum gas oil for second-generation fuel production in FCC units. *Appl. Catal. B Environ.* **2010**, *96*, 476–485. [CrossRef]
- 11. Graça, I.; Lopes, J.M.; Ribeiro, M.F.; Ramôa Ribeiro, F.; Cerqueira, H.S.; de Almeida, M.B.B. Catalytic cracking in the presence of guaiacol. *Appl. Catal. B Environ.* **2011**, *101*, 613–621. [CrossRef]
- Pinho, A.D.R.; de Almeida, M.B.B.; Mendes, F.L.; Ximenes, V.L.; Casavechia, L.C. Co-processing raw bio-oil and gasoil in an FCC Unit. *Fuel Process. Technol.* 2015, 131, 159–166. [CrossRef]
- Pinho, A.D.R.; de Almeida, M.B.B.; Mendes, F.L.; Casavechia, L.C.; Talmadge, M.S.; Kinchin, C.M.; Chum, H.L. Fast pyrolysis oil from pinewood chips co-processing with vacuum gas oil in an FCC unit for second generation fuel production. *Fuel* 2017, 188, 462–473. [CrossRef]

- 14. Huynh, T.M.; Armbruster, U.; Atia, H.; Bentrup, U.; Phan, B.M.Q.; Eckelt, R.; Nguyen, L.H.; Nguyen, D.A.; Martin, A. Upgrading of bio-oil and subsequent co-processing under FCC conditions for fuel production. *React. Chem. Eng.* **2016**, *1*, 239–251. [CrossRef]
- 15. Wang, C.; Venderbosch, R.; Fang, Y. Co-processing of crude and hydrotreated pyrolysis liquids and VGO in a pilot scale FCC riser setup. *Fuel Process. Technol.* **2018**, *181*, 157–165. [CrossRef]
- 16. Wang, C.; Li, M.; Fang, Y. Coprocessing of Catalytic-Pyrolysis-Derived Bio-Oil with VGO in a Pilot-Scale FCC Riser. *Ind. Eng. Chem. Res.* **2016**, *55*, 3525–3534. [CrossRef]
- 17. Lindfors, C.; Paasikallio, V.; Kuoppala, E.; Reinikainen, M.; Oasmaa, A.; Solantausta, Y. Co-processing of Dry Bio-oil, Catalytic Pyrolysis Oil, and Hydrotreated Bio-oil in a Micro Activity Test Unit. *Energy Fuels* **2015**, *29*, 3707–3714. [CrossRef]
- 18. Sauvanaud, L.; Mathieu, Y.; Corma, A.; Humphreys, L.; Rowlands, W.; Maschmeyer, T. Co-processing of lignocellulosic biocrude with petroleum gas oils. *Appl. Catal. A Gen.* **2018**, *551*, 139–145. [CrossRef]
- 19. Wu, L.; Wang, Y.; Zheng, L.; Shi, M.; Li, J. Design and optimization of bio-oil co-processing with vacuum gas oil in a refinery. *Energy Convers. Manag.* **2019**, *195*, 620–629. [CrossRef]
- 20. Wu, L.; Wang, Y.; Zheng, L.; Wang, P.; Han, X. Techno-economic analysis of bio-oil co-processing with vacuum gas oil to transportation fuels in an existing fluid catalytic cracker. *Energy Convers. Manag.* **2019**, *197*, 111901. [CrossRef]
- Ochoa, A.; Vicente, H.; Sierra, I.; Arandes, J.M.; Castaño, P. Implications of feeding or cofeeding bio-oil in the fluid catalytic cracker (FCC) in terms of regeneration kinetics and energy balance. *Energy* 2020, 209, 118467. [CrossRef]
- 22. Naik, D.V.; Karthik, V.; Kumar, V.; Prasad, B.; Garg, M.O. Kinetic modeling for catalytic cracking of pyrolysis oils with VGO in a FCC unit. *Chem. Eng. Sci.* 2017, 170, 790–798. [CrossRef]
- 23. Cruz, P.L.; Montero, E.; Dufour, J. Modelling of co-processing of HDO-oil with VGO in a FCC unit. *Fuel* 2017, 196, 362–370. [CrossRef]
- 24. Gueudré, L.; Chapon, F.; Mirodatos, C.; Schuurman, Y.; Venderbosch, R.; Jordan, E.; Wellach, S.; Gutierrez, R.M. Optimizing the bio-gasoline quantity and quality in fluid catalytic cracking co-refining. *Fuel* **2017**, *192*, 60–70. [CrossRef]
- 25. Ali, A.A.M.; Mustafa, M.A.; Yassin, K.E. A techno-economic evaluation of bio-oil co-processing within a petroleum refinery. *Biofuels* **2018**, 1–9. [CrossRef]
- Mukarakate, C.; Orton, K.; Kim, Y.; Dell'Orco, S.; Farberow, C.A.; Kim, S.; Watson, M.J.; Baldwin, R.M.; Magrini, K.A. Isotopic Studies for Tracking Biogenic Carbon during Co-processing of Biomass and Vacuum Gas Oil. ACS Sustain. Chem. Eng. 2020, 8, 2652–2664. [CrossRef]
- 27. Bhatt, A.H.; Zhang, Y.; Heath, G. Bio-oil co-processing can substantially contribute to renewable fuel production potential and meet air quality standards. *Appl. Energy* 2020, 268, 114937. [CrossRef]
- Cruz, P.L.; Iribarren, D.; Dufour, J. Life Cycle Costing and Eco-Efficiency Assessment of Fuel Production by Coprocessing Biomass in Crude Oil Refineries. *Energies* 2019, 12, 4664. [CrossRef]
- 29. Tristán, C.; Rumayor, M.; Dominguez-Ramos, A.; Fallanza, M.; Ibáñez, R.; Ortiz, I. Life cycle assessment of salinity gradient energy recovery by reverse electrodialysis in a seawater reverse osmosis desalination plant. *Sustain. Energy Fuels* **2020**, *4*, 4273–4284. [CrossRef]
- 30. Delikonstantis, E.; Igos, E.; Augustinus, M.; Benetto, E.; Stefanidis, G.D. Life cycle assessment of plasma-assisted ethylene production from rich-in-methane gas streams. *Sustain. Energy Fuels* **2020**, *4*, 1351–1362. [CrossRef]
- Zhang, X.; Witte, J.; Schildhauer, T.; Bauer, C. Life cycle assessment of power-to-gas with biogas as the carbon source. Sustain. Energy Fuels 2020, 4, 1427–1436. [CrossRef]
- 32. Cruz, P.L.; Iribarren, D.; Dufour, J. Modeling, simulation and life-cycle assessment of the use of bio-oil and char in conventional refineries. *Biofuels Bioprod. Biorefining* **2020**, *14*, 30–42. [CrossRef]
- Mark Goedkoop, R.S. The Eco-Indicator 99: A Damage Oriented Method for Life Cycle Impact Assessment. In *Methology Report*; PRé Consultants: Amsterdam, The Netherlands, 2000.
- Jones, S.; Meyer, P.; Snowden-Swan, L.; Padmaperuma, A.; Tan, E.; Dutta, A.; Jacobson, J.; Cafferty, K. Process Design and Economics for the Conversion of Lignocellulosic Biomass to Hydrocarbon Fuels; U.S. Department of Energy: Oak Ridge, TN, USA, 2013.
- Agblevor, F.A.; Mante, O.; Abdoulmoumine, N.; McClung, R. Production of Stable Biomass Pyrolysis Oils Using Fractional Catalytic Pyrolysis. *Energy Fuels* 2010, 24, 4087–4089. [CrossRef]
- 36. Wu, L.; Liu, Y.; Zhang, Q. Operational Optimization of a Hydrotreating System Based on Removal of Sulfur Compounds in Hydrotreaters Coupled with a Fluid Catalytic Cracker. *Energy Fuels* **2017**, *31*, 9850–9862. [CrossRef]
- 37. Wang, L.; Wu, H.; Hu, Y.; Yu, Y.; Huang, K. Environmental Sustainability Assessment of Typical Cathode Materials of Lithium-Ion Battery Based on Three LCA Approaches. *Processes* **2019**, *7*, 83. [CrossRef]
- 38. Wu, L.; Yang, Y.; Yan, T.; Wang, Y.; Zheng, L.; Qian, K.; Hong, F. Sustainable design and optimization of co-processing of bio-oil and vacuum gas oil in an existing refinery. *Renew. Sustain. Energy Rev.* **2020**, *130*, 109952. [CrossRef]