Article

Screening and Optimization of Microalgae Biomass and Plastic Material Coprocessing by Hydrothermal Liquefaction

Bingfeng Guo,* Boda Yang, Ying Su, Shicheng Zhang,* Ursel Hornung, and Nicolaus Dahmen

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ABSTRACT: In the past decade, microalgae biomass has been attracting considerable interest in valuable biocomponents and biofuel production. Meanwhile, plastic waste handling has become one of the most pressing global environmental concerns. Coprocessing of plastic waste and biomass has previously been reported to produce good quality fuel oil and high-value chemicals. In this study, we examined a coliquefaction process (co-HTL) of 2 microalgae, *Chlorella vulgaris* (Cv) and *Nannochloropsis gaditana* (Ng), with nine types of common plastics. In a first step, the co-HTL process was conducted in microautoclave reactors with a fixed algae/plastic mass ratio (50:50) at a temperature of 350 °C and a pressure of 16 MPa for a holding time of 15 min. Among the different types of plastics, positive synergistic effects between polycarbonate (PC), polystyrene (PS), and microalgae have been observed: (1) Plastics showed greater decomposition. (2) HTL crude oil yields were increased. Ng algae exhibits a higher interaction ability with plastics. Then, PC and PS were coprocessed with Ng algae using the response surface methodology to optimize the effects of temperature (300−400 °C), algae/plastic mass ratio (20:80−80:20), and holding time (5−45 min) on HTL crude oil yield. Software-based data analysis of the co-HTL experiments were conducted, and the optimal parameters were proposed, which were verified by the experiment results; Ng+PC (20:80 wt %) exhibits the highest crude oil yield of 67.2% at 300 °C with a 5 min holding time, while Ng+PS (80:20 wt %) generates 51.4 wt % crude oil yield at 400 °C and a 25 min holding time. Finally, the analytical results of elemental analysis, FTIR, ^{1}H NMR, GPC, GC-MS, and TGA on the crude oil produced from pure microalgae HTL and co-HTL were compared, indicating that Ng+PC crude oil is more suitable for aromatic chemicals production and Ng+PS crude oil could be more favorable for biofuel applications.

KEYWORDS: *microalgae biofuel; waste plastic, coprocessing, hydrothermal liquefaction; synergistic effects*
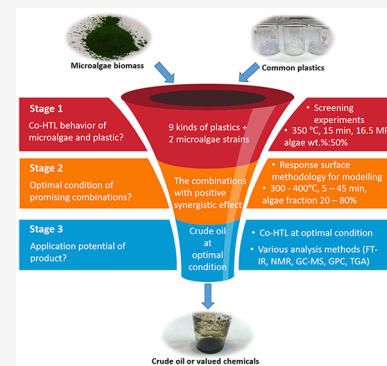
1. INTRODUCTION

Biofuel from renewable and sustainable feedstock is a promising alternative to fossil fuels. Microalgae biomass has been regarded suitable for third generation biofuels, due to its high photosynthetic efficiency (transforming 9%−10% of solar energy into biomass[1]) and its ability to grow rapidly (2- to 10-fold more biomass per unit land area than terrestrial plants[2]) in harsh conditions or municipal/agroindustrial wastewater.[3] The industrial cultivation of microalgae has been increasing in the past decade,[4] as has the public acceptability of algae biofuel. The majority of European experts and stakeholders believe that genetically engineered microalgae could provide strong benefits compared to other fuels,[5] which greatly promotes the potential of microalgae biomass for large-scale biofuel production. For the conversion of high-moisture microalgae, hydrothermal liquefaction (HTL), typically at 260−400 °C and a pressure of 8−20 MPa,[6] is considered to be a suitable thermochemical process,[7] as it eliminates the high cost and energy consumption of drying. Due to the special properties of water in its subcritical condition,[8] HTL can convert microalgae into a variety of primary products,[9] such as aqueous phase, gas

products, solid residues, and crude oil. Subsequently, the crude oil with higher energy density can be upgraded to a variety of liquid hydrocarbon fuels.

Apart from biomass conversion, HTL has also been reported to be capable of decomposing plastic wastes for liquid fuel and valued chemicals.[10,11] It provides an interesting solution for the disposal of rapidly growing amounts of plastic waste, which is regarded as one of the most pressing environmental issues nowadays.[12] In 2019, approximately 368 million tons of plastics were produced worldwide, out of which about 76 wt % plastic waste was landfilled. Only 9 wt % was recycled, and 15 wt % was used for energy recovery via combustion,[10] resulting in detrimental substances such as hydrochloric acid, sulfur dioxide, and heavy metals as well as potentially carcinogenic
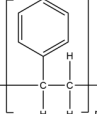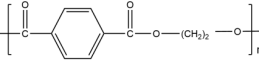
Table 1. Biomass Feedstock Characterization of *Chlorella vulgaris* and *Nannochloropsis gaditana* by Elemental Analysis (wt %), Biochemical Composition (wt %), Ash (wt %), Moisture Content (wt %), and Higher Heating Value (HHV) (MJ/kg)

Strain	C	H	N	S	O[a]	Protein	Lipid	Carbohydrates	Ash	Moisture	HHV
Chlorella vulgaris	47.7	7.5	8.4	0.5	35.9	51.9	23.6	9.2	6.8	3.6	22.03
Nannochloropsis gaditana	46.8	7.8	7.4	0.7	37.3	43.8	18	25.8	11.8	3.5	21.84

[a]By difference $(100 - C - H - N - S)$.

Table 2. Plastic Materials Investigated in This Work

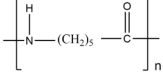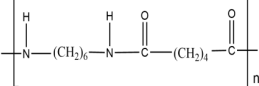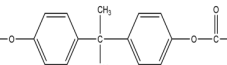| Plastic type	Abbreviation	Structure	Common application in daily life
Polyethylene	PE		Packaging, automotive
Polypropylene	PP		Packaging, textiles
Polystyrene	PS		Packaging, electronics, automotive
Polyethylene terephthalate	PET		Packaging foods and beverages
Poly(vinylchloride) low density	LDPVC		Pipes, bags, membranes
Poly(vinylchloride) high density	HDPVC		Pipes, medical devices, wires, cables insulation
Nylon 6	Nylon 6		Filament yarns, staple fibers
Nylon 66	Nylon 66		Textiles, carpets
Polycarbonate	PC		Room dividers, safety glasses, electronics

emissions. An estimated 4−12 million tons of plastic waste end up in the oceans annually.[13] Thus, more effective management and disposal strategies for plastic wastes are urgently required. As part of the search for a solution for the energy crisis and the white pollution problem, coprocessing of plastic waste and biomass has been raising increased attention over the last years as it would contribute to a circular economy with a lesser environmental impact.[14]

There is some literature on the coprocessing of lignocellulosic biomass (such as beech wood, cellulose, and lignin) with plastic wastes. Plastics could provide hydrogen during thermal coprocessing,[15] and thus, a synergistic effect (SE) exists between biomass and plastics during coprocessing, leading to an enhanced liquid product yield with improved quality.[16−18] Besides, in the presence of biomass, plastic materials can also be decomposed easier by coprocessing. Hongthong et al.[19] studied the co-HTL of common plastics with pistachio hulls, and their results showed the biomass could synergistically

assist the decomposition of plastic. Both polyethylene terephthalate and nylon-6 could be almost completely depolymerized during coprocessing, and high HTL crude yield up to 35 wt % was achieved. This provides evidence of the potential of coprocessing biomass and plastic material. Apart from oil production, the catalytic copyrolysis of lignocellulosic biomass and plastic was also found to produce valuable chemicals such as toluene, xylene, and the respective monomers of the treated polymer.[20] The key to interaction between biomass and plastic is the appropriate overlap of their decomposition ranges. With the help of thermogravimetric analysis, the pyrolysis processes of several types of aquatic biomass have been investigated, and it has been found that the decomposition temperature of plastics and microalgae can be overlapped.[21] This supports the potential of coprocessing microalgae and plastics. Recently, Wu et al.[22] found a maximum synergistic effect leading to an increased yield of 3.3% between microalgae *Dunaliella tertiolecta* and polypropy-

lene during co-HTL when the mass ratio was 80:20, and the addition of polypropylene would significantly affect the transformation pathways of carbohydrates in microalgae, thus improving the bio-oil quality. Raikova et al.[23] also studied the effect of some marine plastic pollutants on the HTL of macroalgae and found that, instead of problematic contaminants, marine nylon debris could present a promising revenue stream via hydrothermal processing in future biorefineries. The production of algae-based biofuel via HTL is not always an energy-efficient process, and the poor quality of crude oil (such as high nitrogen content, low heating value, and high viscosity) renders its direct handling and use[24] in energy and fuel application. By a coliquefaction process of plastic of algae biomass, the obtained crude oil quality is expected to be improved. Furthermore, for a more economical microalgae biorefinery, additional values are supposedly generated along with the microalgae biofuel production.[25] Combining plastics and microalgae in a co-HTL process could not only improve the quality of microalgae biofuel and produce high-value chemicals but could also offer an effective alternative way for plastic waste handling. However, limited studies on this process with microalgae are currently available. Algae and plastics have very different chemical compositions and thermal decomposition behaviors, so searching for suitable materials for the co-HTL process is therefore essential.

In this work, the goal was to assess the co-HTL process of two microalgae species and a wide range of commonly used plastics in view of their potential for the improvement of liquid product yield and quality. After screening with fixed conversion parameters, the response surface methodology was applied to optimize the co-HTL crude oil production. Furthermore, the composition of the co-HTL crude oil product was examined, and its possible applications for chemical and energetic use were evaluated.

2. MATERIALS AND METHODS

2.1. Microalgae Strains and Plastics. *Chlorella vulgaris* (Cv) and *Nannochloropsis gaditana* (Ng) are known to be fast-growing microalgae and are genetically easy to manipulate, making them promising candidates for the production of biodiesel;[26] they were selected as the microalgae feedstock in this work. Cv algae were obtained in dry powder form from Roquette Klötze GmbH (Germany). Ng algae dry powder was purchased from Astaxa GmbH (Germany). The elemental and biocomponent characterizations of the feedstock are given in Table 1.

For the plastic waste representatives, nine types of commonly used plastics have been selected as the model component in order to explore the co-HTL behavior of each kind of plastic. They were obtained from Sigma-Aldrich in the form of granulate (approximately 3 mm), as shown in Table 2.

2.2. Experimental Procedure. Three sets of experiments have been performed for this work. First, all combinations of the different types of plastics and microalgae went through a screening co-HTL process with the fixed algae/plastic mass ratio of 50:50 at a reaction temperature of 350 °C, a pressure of 16 MPa, and a holding time of 15 min. The algae/plastic combinations with a good positive synergistic effect were further investigated in a next step, employing the response surface methodology (RSM) to optimize the process. In total, 20 experiments were designed to study the effects of three independent variables (HTL temperature, HTL holding time, and algae/plastic ratio) on the HTL crude yield. The

investigating ranges of the three variables were selected as 300−400 °C, 5−45 min, and 20−80 wt % (algae mass), respectively. The optimal HTL conditions were suggested by the RSM model. Finally, the HTL crude was produced at the suggested optimal set of parameters for the positive combinations and subjected to various analytic characterizations to obtain further insights into the co-HTL crude oil properties and probe its further application options.

2.3. Co-HTL Process and Product Separation. The co-HTL of microalgae with plastics was carried out in a 25 mL batch microautoclave reactor, made of EN 1.4571 stainless steel. The HTL temperature of 350 °C and 15 min holding time was selected as the operating conditions for the screening experiments, as they can be considered the most typical HTL conditions for producing high crude oil yields from microalgae.[7,27] The mass ratio of microalgae/plastic was maintained as 50:50, and the microalgae/water slurry for co-HTL contained 10 wt % dry mass. Thus, 10 mL of microalgae slurry and 1 g of plastic were put into the autoclave for each run. For comparison, individual HTL experiments were also performed, in which 2 g of pure algae or pure plastics were subjected to HTL alone in the autoclave at the same conditions. Before sealing, the microautoclave was purged and preloaded with nitrogen at a pressure of 5 bar to remove the residual air. Afterward, a GC oven (Agilent, Hewlett-Packard 5890 Series II, USA) was employed for heating. Heating to the target temperature of 350 °C took approximately 18.5 min, following which the autoclaves were maintained at 350 °C for a holding time of 15 min before ice cooling. In the 20 experiments and experiments at optimized conditions, a total of 2 g dry mass was put into the microautoclave, while the microalgae mass fraction was controlled from 20 to 80 wt % at different experimental runs. A heating fluidized sand bath (SBL-2, TECHNE, UK) was used instead of a GC oven in order to minimize the heating time.

After the co-HTL process, the autoclave was opened while connected to a gas collection system; the mass of the gaseous product could be determined using the ideal gas equation and the measured pressure. The composition of the gaseous product was determined by gas chromatography (GC). The other products, the HTL crude, aqueous phase, and solid residue, were separated using vacuum filtration; 35 mL of dichloromethane (DCM) was added into the autoclave and filtrated using a Whatman nylon membrane filter (pore size 0.45 μm). The solid residue was collected on the filter and dried in an oven at 105 °C overnight for gravimetric measurement. As for the liquid products, the filtrate was separated into two phases after a resting period of 30 min, and the DCM phase (with crude oil dissolved) was extracted from the filtrate using a syringe and placed under N_2 flow for 24 h. When there are no more weight changes, the obtained substance is the crude oil product. The rest of the filtrate is the aqueous product.

The product yield calculation is based on the dry mass loaded into the autoclave (microalgae + plastic) according to eq 1. Each HTL experiment run was repeated three times, and the mean values were reported with their standard deviation.

$$\text{Yield}_i \, (\text{wt \%}) = \frac{m_i}{m_{\text{microalgae + plastics (dry mass)}}} \quad (1)$$

where i is the product fraction (HTL crude, gas, solid residues).
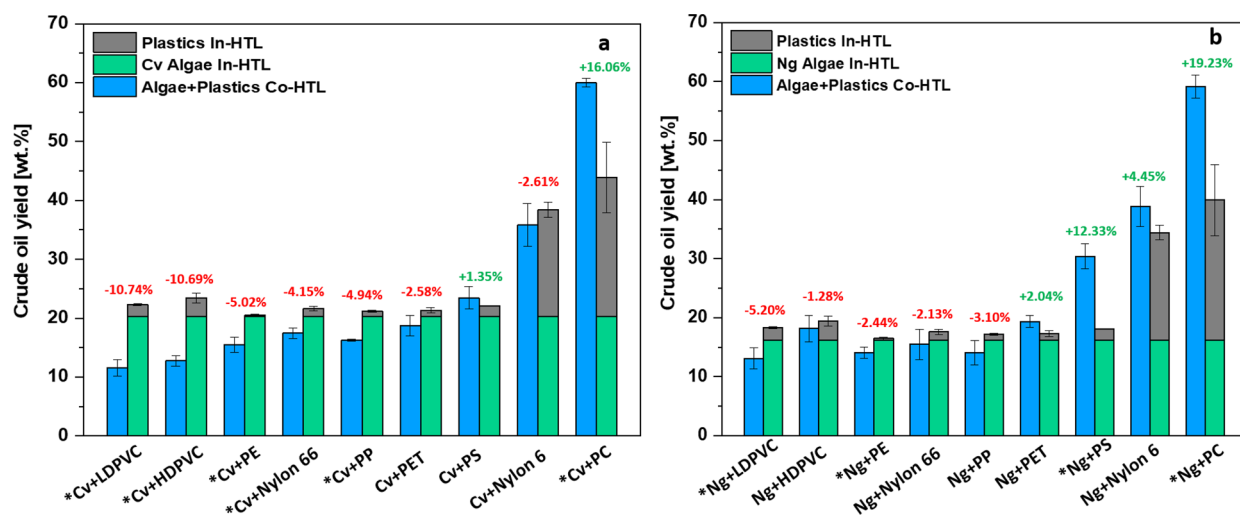
Figure 1. Crude oil yield and synergistic effect of microalgae (a, Cv algae; b, Ng algae) with plastics at co-HTL and individual HTL (In-HTL) at a mass ratio of 50:50. Green numbers signify a positive effect on the overall process. The groups with a p value < 0.05 have been marked with an $*$.

The synergistic effect (SE) of the interaction between microalgae and plastics is calculated by eq 2. It is evaluated with regard to crude oil production and solid decomposition.

$$\text{Synergistic effect} = Y_{\text{co-HTL}} - (R_{\text{microalgae}} \times Y_{\text{microalgae}}$$
$$+ R_{\text{plasics}} \times Y_{\text{plasics}}) \tag{2}$$

where $Y_{\text{co-HTL}}$ is the yield of crude oil or solid residues obtained in the co-HTL experiments, and R is the mass ratio of microalgae or plastics in the total mass, while $Y_{\text{microalgae}}$ and Y_{plastics} are the yields of crude oil or solid residues in their individual HTL experiments, respectively.

2.4. Analysis of co-HTL Product. For analysis of the microalgae feedstock and co-HTL products, various techniques were applied to shed light on the product properties. Here, 50 mg of microalgae biomass and a crude oil sample was used for the elemental analysis (EA) with a Vario EL Cube Analyzer (Elementar Analysensysteme GmbH, Germany). The content of O was calculated by difference ($100 - C - H - N - S$), and Boie's formula (eq 3) was applied for the calculation of the higher heating value (HHV).

$$\text{HHV (MJ/kg)} = 0.3516 \times C + 1.16225 \times H$$
$$- 0.1109 \times O + 0.0628 \times N + 0.10465 \times S \tag{3}$$

For the carbon balance evaluation of the co-HTL process, the total inorganic carbon (TIC) and total carbon (TC) were determined for the HTL aqueous product using a DIMATOC 2100 instrument. The total organic carbon (TOC) was calculated by difference, TOC = TC − TIC. The composition of the HTL gas product was analyzed using gas chromatography (Agilent GC 7890A, USA) equipped with a flame ionization detector (FID) and a back thermal conductivity detector (TCD) in series and Porapak Q and Molsieve columns, respectively. Fourier-transform infrared spectroscopy (FT-IR) spectra on the crude oil were measured with a Varian 660-IR spectrometer (Shimadzu, Japan). A standard KBr pressing served as a background matrix for the scans at wavelengths ranging from 400 to 4000 cm^{-1} and was averaged over eight replicate scans. For the proton nuclear magnetic resonance analysis (^{1}H NMR), 100 mg of the crude oil sample was dissolved in 800 μL of methanol-D4, and solution samples

were loaded to the Varian 400 MHz NMR system. A typical spectrum of the crude oil sample was acquired at 400 MHz across 256 scans per ^{1}H spectrum, with a spectral width of 6398.5 Hz (16 ppm, transmitter offset of 399.9 giving spectra from −2 to 14 ppm). The chemical shifts, measured in ppm and relating to different resonating protons in functional groups, were analyzed with the MestReNova software. Gel permeation chromatography (GPC) was applied to crude oil samples using a Merck Hitachi DAD L-2455 with an RI detector L-2490 for determining the molecular weight distribution. Dimethyl sulfoxide (DMSO) as the eluent and an A2500 aqueous column (300 mm × 8 mm) (Malvern Panalytical) were used. The GC-MS (Agilent 6890N equipped with a 5973 network mass selective detector) system was used for the identification of compounds in the crude oil. About 100 mg of crude oil sample was dissolved into 1 mL of THF, and after filtration, the probe was further diluted by a factor of 10.5 μL of sample injected in splitless mode at 280 °C with the following thermal program: 70 °C for 2 min, then 8 °C/min to 180 °C, then 4 °C/min to 280 °C, and then hold for 10 min. An RTx-5MS column (0.25 mml D, 0.25 df) was equipped with helium as the carrier gas at a flow rate of 1.5 mL/min. The data analysis was performed with qualitative analysis with MassHunter Acquisition 10.0 with the database of the National Institute of Standards and Technology (NIST17). Then, 20 mg of crude oil sample was subjected to thermogravimetric analysis (TGA, Mettler Toledo 2LF, USA) at an N$_2$ flow of 50 mL/min and a heating rate of 10 °C/min from 25 to 800 °C.

3. RESULTS AND DISCUSSION

3.1. Screening Experiments. *3.1.1. Crude Oil Yield and Synergistic Effect.* The most important key feature of a fuel process is the crude oil yield. Figure 1 shows the crude oil yield of different algae/plastics combinations from the screening experiments and the corresponding synergistic effect (SE). The crude oil yield of co-HTL and the sum of 50% crude oil yield of microalgae and plastic in each individual HTL (In-HTL) were compared. A t test by GraphPad was performed, and a p value was determined to see if there is a statistically significant difference between the means of two groups. It can be seen that PET, PS, Nylon 6, and PC showed a positive SE in co-HTL with Ng algae, while in the case of Cv algae only PS and
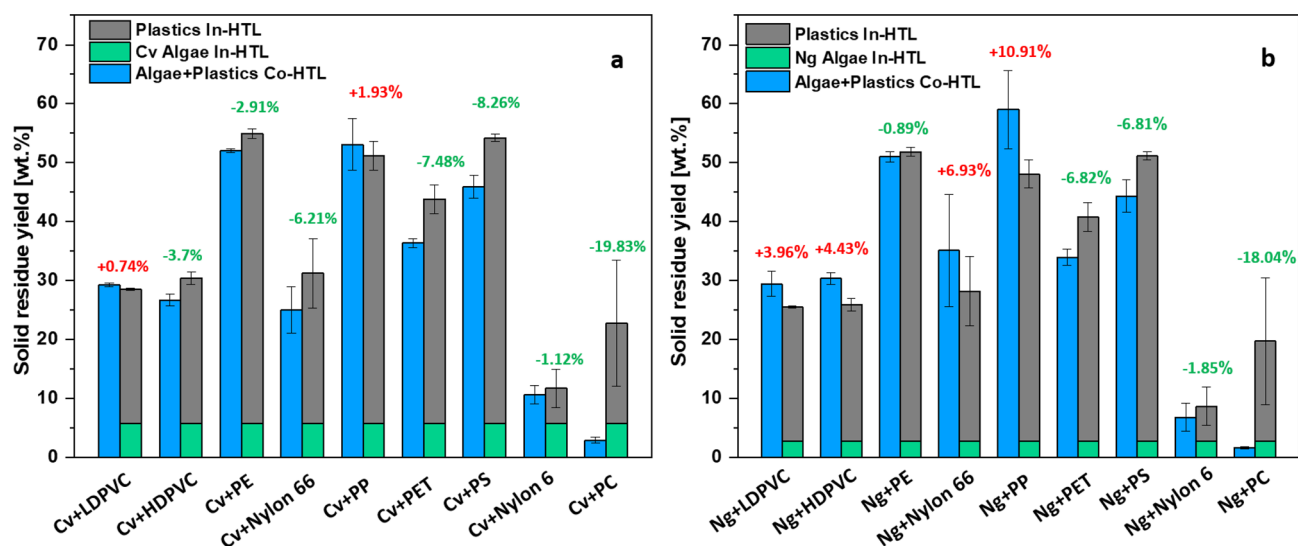
Figure 2. Yield of the solid residue and corresponding synergistic effect of microalgae (a, Cv algae; b, Ng algae) with plastics during co-HTL and individual HTL (In-HTL) at a mass ratio of 50:50. Green numbers signify a positive effect on the overall process.
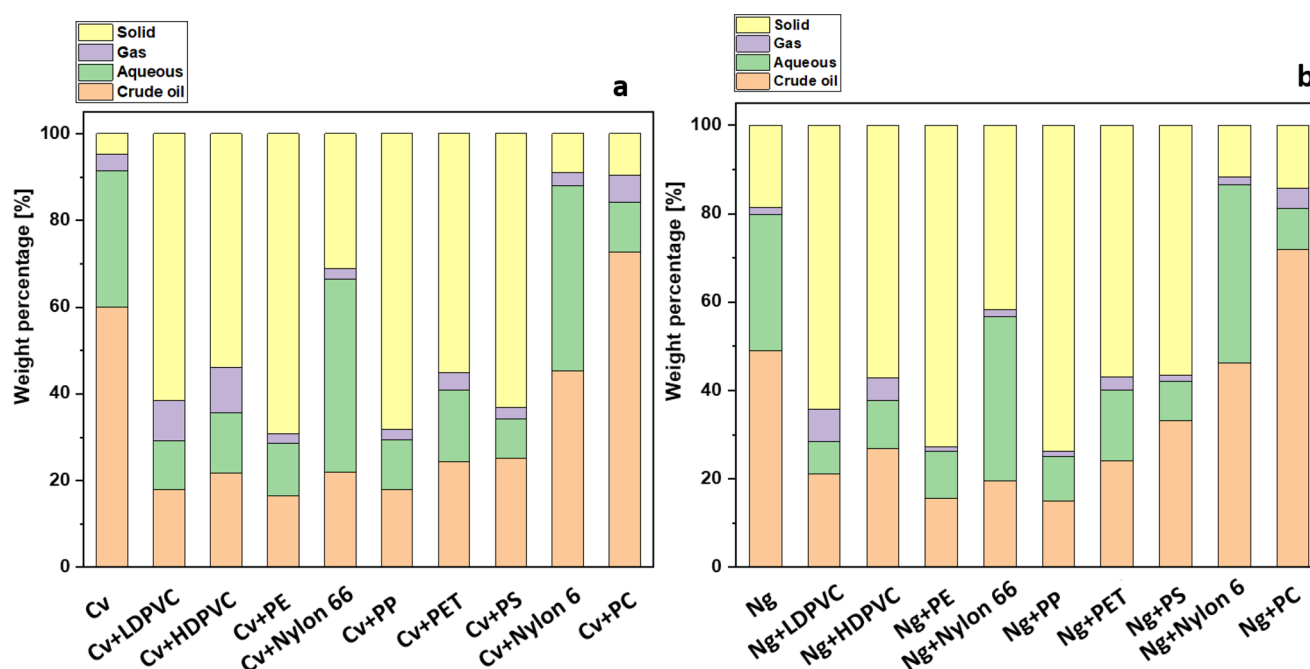
Figure 3. Carbon balance of co-HTL process (a, Cv algae; b, Ng algae). The solid fraction is obtained by the difference C (solid) = 100 − C (crude oil) − C (aqueous) − C (gas).

PC showed a positive SE. Moreover, the SE with Ng algae was generally larger than that of Cv algae, indicating that Ng algae interact better with plastics during co-HTL. This could be caused by the higher carbohydrate content of Ng algae. It has been reported[22] that the addition of some plastics would change the decomposition route of carbohydrates and thus promote Maillard reactions to form more liquid product. Besides, the PE, Nylon 66, PP, and PET showed almost no decomposition at the investigated HTL conditions; the major reaction was HTL of the microalgae, which is known to include hydrolysis, decarboxylation, dehydration, depolymerization, and repolymerization.[28] The existence of unreactive plastics could reduce the contact between microalgae and water, thus resulting in a negative SE. Besides, the HTL of LDPVC and HDPVC would generate an acidic product,[29]

which would cause an increase in charring reactions. It should therefore be avoided in HTL.

3.1.2. Solid Residues Yield. The solid residues reflect the extent to which microalgae and plastics can assist each other in the decomposition during co-HTL. As shown in Figure 2, for the co-HTL of PE, PET, PS, Nylon 6, and PC with both microalgae systems, less solid residue is generated than in the individual HTL conversions. As the solids are mainly residual plastic material (by virtual observation), it can be concluded that the existence of microalgae would generally promote the decomposition of these plastics during HTL. Unlike the trend in crude oil, Cv algae present an overall better effect on the decomposition of plastics than Ng algae. This phenomenon would provide an interesting strategy for plastic waste treatment using microalgae as assistance to lower the severity

Table 3. Design and Results of Experiments

	Process Parameters			Ng algae+PC		Ng algae+PS	
Run	Temperature (°C)	Holding time (min)	Algae mass ratio (wt %)	Crude oil yield (wt %)	Solid residue yield (wt %)	Crude oil yield (wt %)	Solid residue yield (wt %)
1	350	5	50	55.3 ± 3.6	1.6 ± 0.8	14.6 ± 2.4	52.8 ± 2.5
2	400	5	20	57.2 ± 2.8	1.2 ± 0.4	46.4 ± 4.7	47.8 ± 4.4
3	300	25	50	54.8 ± 4.6	2.1 ± 0.4	17.8 ± 3.1	52.8 ± 3.9
4	350	25	20	58.8 ± 2.6	1.8 ± 0.1	15.2 ± 2.8	72.7 ± 2.6
5	300	5	20	67.2 ± 4.3	6.5 ± 3.1	7.1 ± 3.7	79.2 ± 3.0
6	400	25	50	49.5 ± 1.9	3 ± 0.1	44.5 ± 0.9	2.1 ± 0.1
7	325	35	80	46.9 ± 2.1	3.5 ± 0.4	37.2 ± 7.6	16.5 ± 7.6
8	300	15	80	49.2 ± 0.8	3.4 ± 0.2	33.3 ± 3.1	22.5 ± 3.1
9	400	45	20	53.2 ± 1.9	2.5 ± 0.3	42.6 ± 9.8	0.7 ± 0.1
10	350	25	20	59.7 ± 1	1.9 ± 0.2	16.1 ± 3.2	72.5 ± 1.9
11	350	5	50	59.4 ± 3.1	2.5 ± 0.1	15.7 ± 0.8	50.2 ± 0.4
12	325	15	35	46.9 ± 1.7	2.8 ± 1.4	18 ± 1	60.7 ± 2.2
13	350	25	20	60.8 ± 0.8	1.8 ± 0.2	12 ± 2.1	75.4 ± 3.8
14	400	45	50	40.9 ± 2.6	3.4 ± 0.4	32.8 ± 1	3.5 ± 0.8
15	375	45	80	41.6 ± 0.5	4.2 ± 0.3	42.8 ± 3.0	4.1 ± 0.2
16	300	45	50	57.9 ± 0.9	2.3 ± 0.1	22.6 ± 0.7	51.4 ± 0.4
17	400	5	80	49.3 ± 0.9	3.4 ± 0.1	51.4 ± 2.5	4.9 ± 2.1
18	400	5	50	57.1 ± 2.6	3.1 ± 0.3	32.5 ± 3.5	36.5 ± 2.8
19	400	25	50	51.4 ± 1.4	3.1 ± 0.1	44.3 ± 0.8	2 ± 0.2
20	300	45	50	58.7 ± 1.3	2.3 ± 0.8	21.9 ± 0.5	51.7 ± 0.2

of reaction conditions. A possible explanation is the formation of organic acids from microalgae during HTL, which could have a staining effect on the plastic surface, facilitating the breakdown of polymers.

3.1.3. Carbon Balance. In order to better evaluate the entire process, a carbon flow balance has been calculated, based on the product yields and elemental analysis of the crude oil, TOC analysis of the aqueous phase, and GC analysis of the gas product. As presented in Figure 3, the trends in both algae are quite similar; approximately 60 and 44 wt % of the carbon can be transferred from microalgae to the crude oil phase of Cv and Ng, respectively. In most cases, the addition of plastics would lead to a lower carbon percentage in the crude oil phase, mainly because PE, Nylon 66, PP, and PET could not be decomposed at the applied conditions. LDPVC and HDPVC have more solid residues as a result of charring reactions,[30] making these two plastics unsuitable for co-HTL. In the cases of Nylon 6 and Nylon 66, about 40 wt % of the carbon remained in the aqueous phase. For both algae, the addition of PC promoted a higher carbon fraction (around 70 wt %) in the crude oil phase, considering the high crude oil yield and low solid yield of PC at co-HTL. PC is thus suggested as the most suitable plastic material for the co-HTL process.

Another promising plastic found by the results above is PS, as it also presents a high crude oil yield and good SE. As discussed above, for crude oil production, Ng algae have a better interaction ability than Cv algae. Therefore, both PS and PC together with Ng algae were selected for further optimization experiments.

3.2. Optimization of co-HTL Process. *3.2.1. Experimental Results.* The response surface methodology (RSM) as an experimental design technology using central composite design (CCD) was used to evaluate the effects of these three variables on the co-HTL crude oil yield and their interactions. RSM is a representative method for generating meta models. The original model is evaluated at multiple sample points, and the meta model is usually designed as a linear or a quadratic

function. Table 3 shows the experiment design as well as the crude oil and solid residue yield of each run. It was noted that the Ng+PC crude oil yield ranged between 40 and 67 wt %, while Ng+PS yields ranged from 7 to 51 wt %. This indicates that the Ng+PS combination is more susceptible to the experimental parameters. The same trend is observed with regard to the solid residue yield. The solid residues of Ng+PC remained at a low level (less than 4 wt %) in all runs, while Ng+PS yields ranged from almost zero to 80 wt % solids.

3.2.2. Analysis of Experimental Data. Response surface models of crude oil yield were developed based on the results obtained from 20 experiments. ANOVA was applied to investigate the effect of reaction parameters and their interaction on the response of crude oil yield; the results of ANOVA are shown in Tables 4 and 5. Two parameters of F and p values indicate if the condition parameters and their interactions as well as the model are significant. A higher F

Table 4. ANOVA Table of Ng+PC Obtained with Response Surface Methodology

Source	Sum of squares	df	Mean square	F value	p value
Model	652.12	10	65.21	4.05	0.0234
A, temp.	137.03	1	137.03	8.51	0.0171
B, time	44.66	1	44.66	2.77	0.1302
C, algae fraction	301.86	1	301.86	18.74	0.0019
AB	72.14	1	72.14	4.48	0.0634
AC	0.0530	1	0.0530	0.0033	0.9555
BC	0.0418	1	0.0418	0.0026	0.9605
A^2	4.26	1	4.26	0.2645	0.6195
B^2	6.41	1	6.41	0.3979	0.5439
C^2	4.89	1	4.89	0.3036	0.5951
ABC	7.32	1	7.32	0.4543	0.5172
Residual	144.98	9	16.11		
Error	0	5	0		
Cor total	797.10	19			

Table 5. ANOVA Table of Ng+PS Obtained with Response Surface Methodology

Source	Sum of squares	df	Mean square	F value	p value
Model	3368.74	9	374.30	18.79	<0.0001
A, temp.	1451.40	1	1451.40	72.84	<0.0001
B, time	60.08	1	60.08	3.02	0.1131
C, algae fraction	694.96	1	694.96	34.88	0.0001
AB	65.90	1	65.90	3.31	0.0990
AC	84.42	1	84.42	4.24	0.0666
BC	20.47	1	20.47	1.03	0.3347
A^2	437.08	1	437.08	21.94	0.0009
B^2	31.86	1	31.86	1.60	0.2348
C^2	239.26	1	239.26	12.01	0.0061
Residual	199.26	10	19.93		
Error	0	5	0		
Cor total	3567.99	19			

statistic value indicates a more significant effect on the HTL crude yield,[31] and it can be noted that the significance order of reaction parameters on the crude oil yield in Ng+PC is algae/plastic mass ratio > HTL temperature > holding time. For Ng+PS, the significance order is HTL temperature > algae/plastic mass ratio ≫ holding time. This indicates that HTL of Ng and PS is a fast and stable reaction; the long holding time has nearly no effect on the crude oil yield.

Figure 4 shows the 3D response surface of crude oil yield at different reaction conditions. Different features have been found with these two surfaces; a lower algae fraction was found to generate more crude oil for the Ng+PC combination, while a higher algae fraction lead to more crude oil for the Ng+PS combination. The HTL temperature and holding time also played a different role in both combinations; lower HTL temperatures and shorter holding times are more favorable for crude oil production in the Ng+PC combination, showing that more repolymerization reactions take place between Ng algae and PC over a longer period of time. In the case of Ng+PS, about 40 wt % of crude oil yield can be achieved at 300 °C; however, with increasing temperature, the yield initially drops before it begins to increase constantly after passing 350 °C. The reason could be that the PS plastic started to decompose and interact with microalgae after passing 350 °C, making a positive contribution to the crude oil yield. In general, higher temperature leads to more crude oil in the Ng+PS

combination, and the holding time seems to be insignificant, as suggested by ANOVA results.

Besides, the coded eqs 4 and 5 of the crude oil yield were proposed using design expert software, in which factor A stands for HTL temperature, B for holding time, and C for algae fraction ratio. The coded equations are useful for identifying the relative impact of the factors by comparing the factor coefficients. The coefficient of determination (R^2) calculated for eqs 4 and 5 are 0.81 and 0.94, respectively. This confirms that the suggested modified cubic and quadratic equations could generally be used to investigate the impact of these three factors on Ng+PS combination crude oil yield.

$$\text{Ng+PC crude oil yield} = 50.21 - 3.51A - 2.08B - 6.21C$$
$$- 3.32AB + 0.1425AC + 0.1285BC + 1.17A^2 + 1.37B^2$$
$$+ 1.13C^2 - 2.22ABC \tag{4}$$

$$\text{Ng+PS crude oil yield} = 19.16 + 11.19A + 2.41B$$
$$+ 8.83C - 2.96AB - 4.15AC + 2.05BC + 11.45A^2$$
$$- 2.95B^2 + 7.47C^2 \tag{5}$$

Based on the RSM evaluation, the optimal condition for the Ng+PC combination can be suggested as 300 °C, 5 min, and 20 wt % algae fraction, and the Ng+PS combination is suggested for operation at 400 °C, 25 min, and 80 wt % algae fraction for maximum crude oil yield.

3.3. Cohydrothermal Liquefaction at Optimal Conditions and Product Characterization. Co-HTL experiments of two promising plastics and pure microalgae have been further verified at the suggested optimal conditions. Figure 5 shows the product yields and the corresponding SE obtained from co-HTL carried out at these optimal conditions. Ng+PC proved to have a high crude oil yield of 67 wt % with a significant high SE of +50.47%, and it was found that the existence of only 20 wt % Ng algae greatly promoted the decomposition of PC plastic into crude oil. In comparison to the screening experiments, the co-HTL process shows a reduction of more than 64% in solid residue when compared to in-HTL. This phenomenon could assist the degradation of plastics where it is difficult to decompose them individually. Applying microalgae biomass as an additive for plastic waste decomposition could be an interesting idea. A high crude oil yield of about 51.4 wt % was obtained with Ng+PS with a slight 5.6% SE, which is because the PS plastic and microalgae
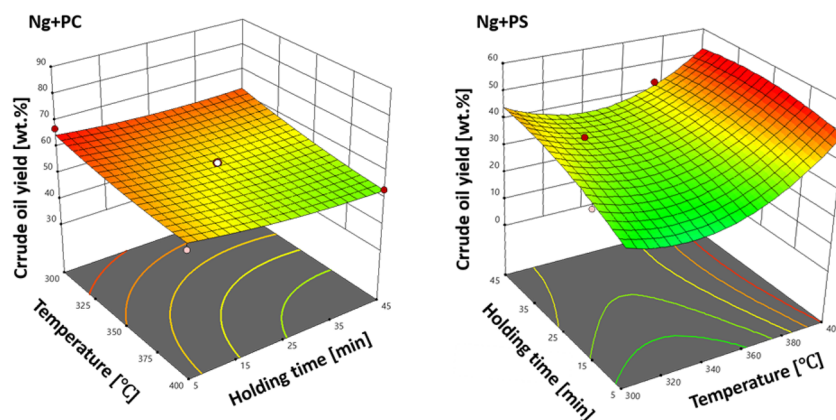
Figure 4. Response surface for crude oil yield (Ng+PC algae fraction, 20 wt %; Ng+PS algae fraction, 80 wt %).
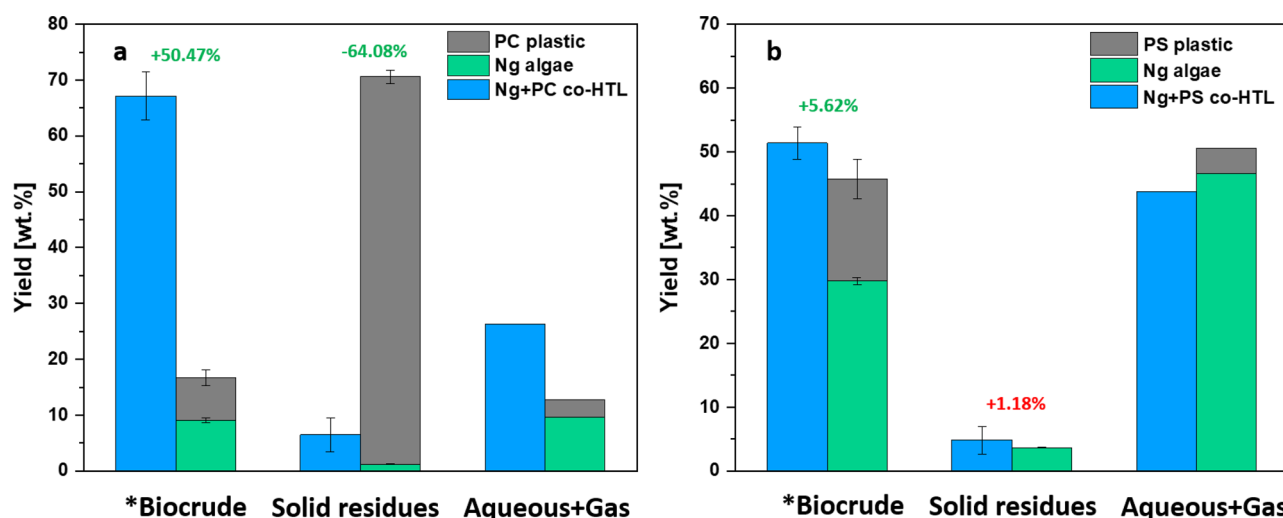
Figure 5. Product yield of co-HTL and in-HTL at the suggested optimal conditions (a, Ng+PC; b, Ng+PS). Green numbers signify a positive effect on the overall process. The groups with a *p* value < 0.05 have been marked with an ∗.

had already been decomposed to a large extent during their in-HTL. The crude oil yields are a close match to the theoretical value of 64.8 and 49.5 wt % suggested by the evaluation tool, confirming that the obtained models describe the co-HTL process quite well.

The elemental analysis of crude oil and HHV are shown in Table 6. Compared to Ng 300 °C, Ng+PC crude oil undergoes

**Table 6. Elemental Composition of Crude Oil Sample and Higher Heating Value (HHV) in MJ/kg**

Samples	C (wt %)	H (wt %)	N (wt %)	S (wt %)	O[a] (wt %)	HHV (wt %)
Ng, 300 °C	69.7	8.5	6.5	0.6	14.7	33.22
Ng+PC	75.2	6.9	0.8	0.1	17	32.63
Ng, 400 °C	76.8	9.1	5.6	0.5	8	37.09
Ng+PS	78.6	8.3	3.9	0.5	8.7	36.61

[a]By difference $(100 - C - H - N - S)$.

a great change in its elemental composition (less nitrogen, sulfur, and hydrogen), since the majority of the crude oil is derived from PC plastic. On the other hand, Ng+PS crude oil has a similar elemental composition to the crude oil from pure Ng algae. Therefore, similar properties can be expected. The N content was reduced in both cases, and by addition of plastics, the conversion pathway could be changed to transfer more N into aqueous phase or solid residue phase. To shed light on the properties of crude oil products, various further analytic measurements were applied.

3.3.1. Fourier-Transform Infrared Spectroscopy. FTIR measurement was performed to reveal the functional group changes between crude oil from pure microalgae and co-HTL at the optimal conditions. Figure 6a shows FTIR spectra of co-HTL crude with PC and of Ng algae. The peaks around 2850 and 2970 cm^{-1} (aliphatic C−H vibrations[32]) and the peak at around 1700 cm^{-1} (attributed to aldehydes, ketones, and carboxylic acids[33]) vanish in the Ng+PC sample, while the peak at 1600 cm^{-1} (aromatic rings) became more significant, which indicates that more aromatic compounds were generated in the co-HTL product sample. In the Ng+PS crude oil (Figure 6b), no significant change was observed
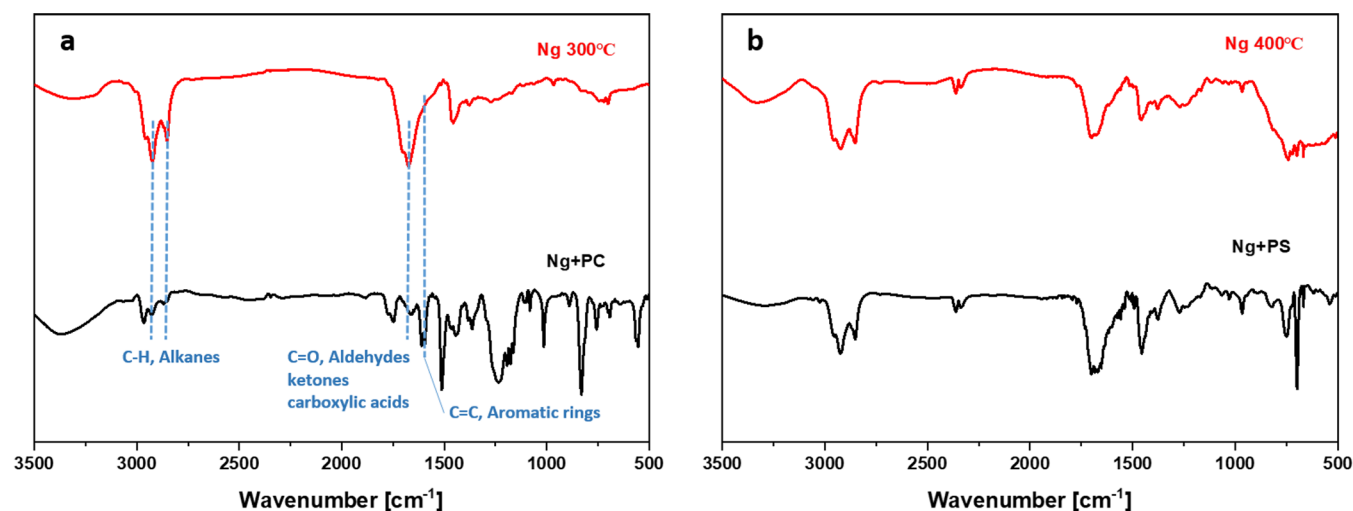
Figure 6. FTIR result of crude oil produced from pure microalgae and microalgae/plastic mixture at their optimal HTL conditions (a, Ng+PC, 20:80; b, Ng+PS, 80:20).
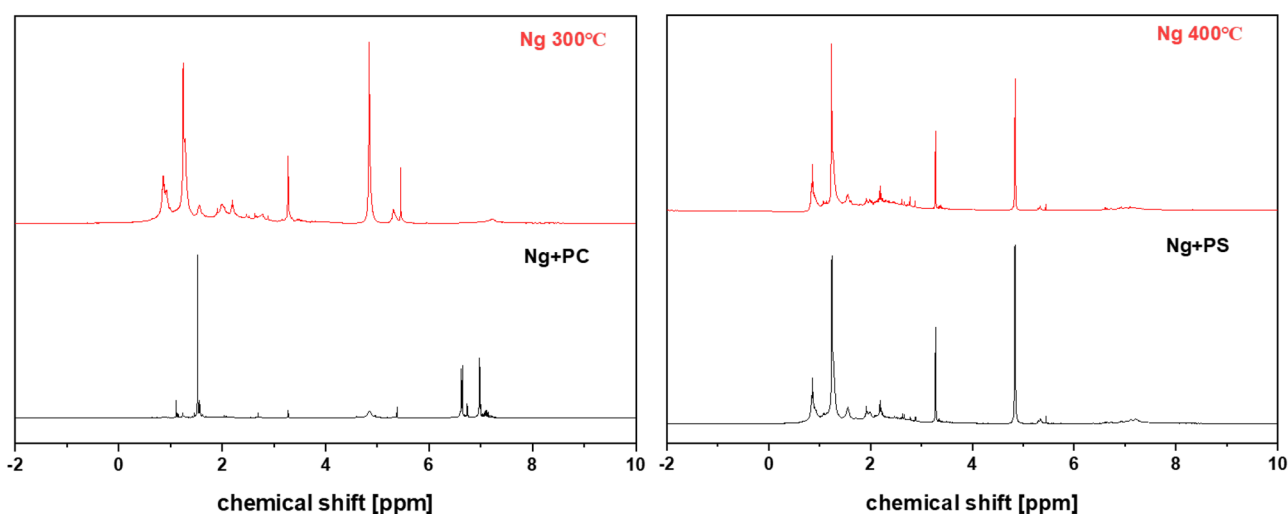
Figure 7. ^{1}H NMR spectra of crude oil.

Table 7. Relative Peak Area Percentage (%) of Different H Type Groups in HTL Crude Oil

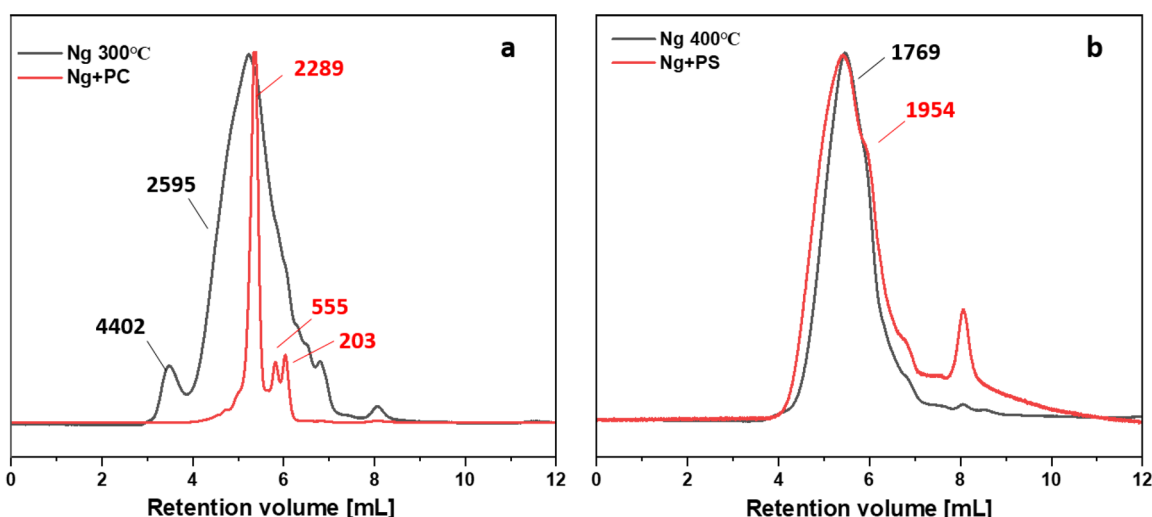|	Alkanes, 0.5−1.5 ppm (%)	Aliphatics, 1.5−3 ppm, (%)	Alcohols, 3−4.4 ppm, (%)	Carbohydrates, 4.4−6 ppm, (%)	Aromatics, 6−8.5 ppm (%)
Ng, 300 °C	43.7	26.6	7.8	19.2	2.6
Ng+PC	21.5	18.7	−	14	45.7
Ng, 400 °C	45.6	38.3	5.9	7.3	2.7
Ng+PS	44.8	30	7.2	12.6	5.4

Figure 8. Main peaks and corresponding average molar weight (Da) of crude oil produced from pure microalgae and microalgae/plastic mixture at their optimal HTL conditions.

compared to the pure Ng sample. This means that the major constituents are similar in both samples. The addition of PS would increase the crude oil yield without changing its composition.

3.3.2. ^{1}H-Nuclear Magnetic Resonance. The information about H atom types in the crude oil was revealed by ^{1}H NMR, as shown in Figure 7. The peak areas have been classified into five groups;[34] 0−1.5 ppm represents the H atoms in alkanes or fatty acids, 1.5−3 ppm the H atoms in aliphatics, 3−4.4 ppm the H atoms in alcohols, 4.4−6 ppm the H atoms in carbohydrates, and 6−8.5 ppm the H atoms bonded to aromatic compounds. The spectrum of Ng+PC has more peaks than Ng 300 °C in the range of 6−9.5 ppm, while Ng 400 °C and Ng+PS are nearly identical. The percentages of peak areas

are given in Table 7. Compared to the crude oil from pure Ng algae at 300 °C, the Ng+PC crude oil has a 22% and 8% lower area in the alkanes and aliphatics areas, respectively, and the area of aromatic groups has been significantly increased from 2.6% to 45.7%. This confirms that Ng+PC crude oil is rich in aromatic compounds. While in the case of Ng+PS the alkanes and aliphatics area shows almost no changes, a slight increase can be observed in the carbohydrates and aromatics area. This supports that the Ng+PS crude oil has similar properties to pure Ng crude oil at 400 °C.

3.3.3. Gel Permeation Chromatography. Figure 8 presents the mass distribution and average molar weight in the crude oil determined by GPC measurement. It is clearly visible that the molar mass distribution in the Ng+PC sample is less broad
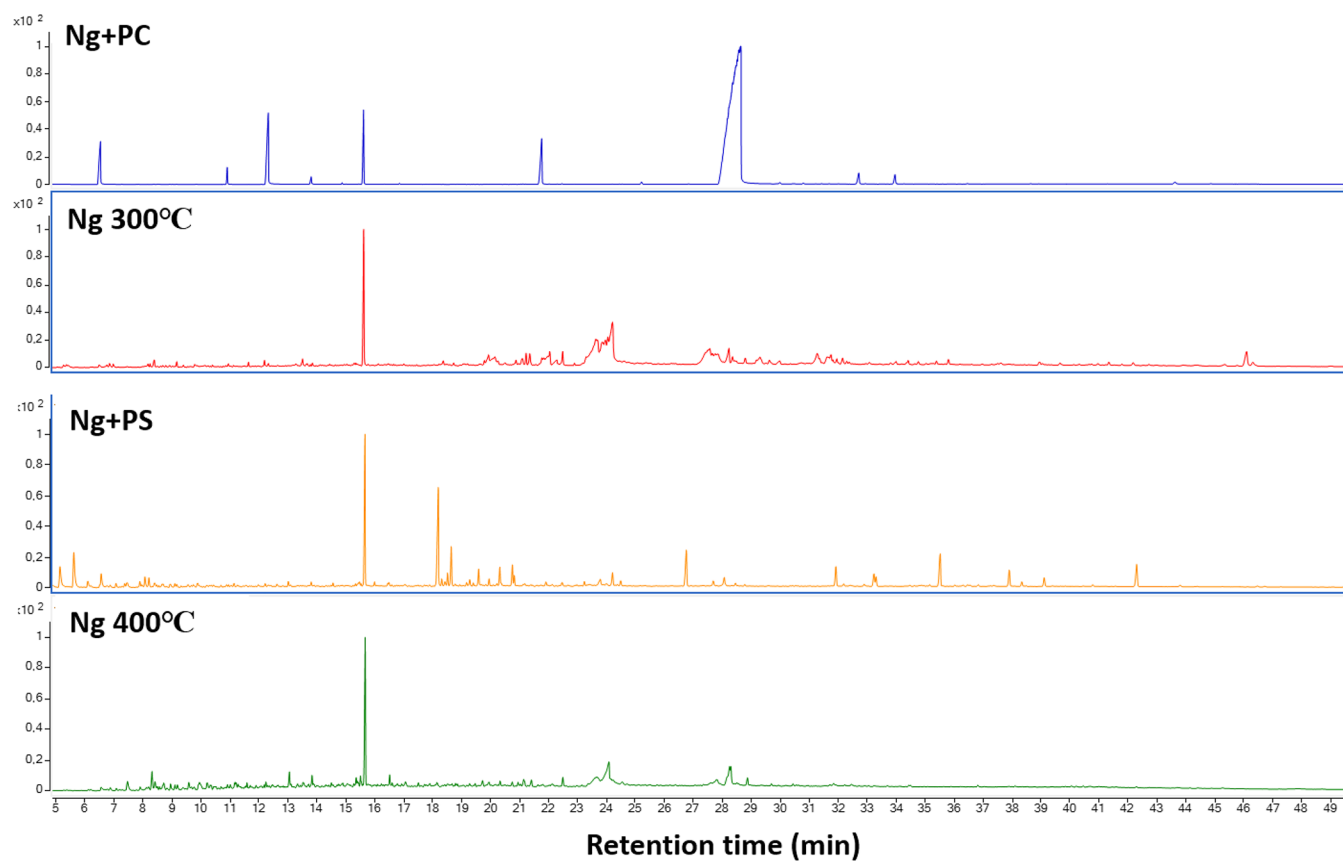
Figure 9. Total ion chromatograms of crude oil.

Table 8. Major Compounds in co-HTL Crude Oil

Ng+PC crude oil			Ng+PS crude oil (retention time 18-21 min)		
Compound	Structure	Content	Compound	Structure	Content
P-Isopropenylphenol		17.7%	Benzene, 1,1'-(1,3-propanediyl) bis-		3.7%
Phenol		10.1%	Benzene, 1,1'-(1-methyl-1,3-propanediyl) bis-		3.7%
Phenol, 4-(1-methyl-phenylethyl)-		9.6%	Benzene, 1,1'-(3-methyl-1-propene-1,3-diyl) bis-		1.7%
p-Cumenol		2 %	Benzene, 1,1'-(1,4-butanediyl) bis-		0.6%
Phenol, 4-ethyl-2-methoxy-		1.1%			

Table 9. Oil Type Distribution of Crude Oil

	Carbon range (Distillation range)						
	C1−C9 (<70 °C)	C5−C10 (70−120 °C)	C10−C16 (120−170 °C)	C14−C20 (170−250 °C)	C20−C50 (250−500 °C)	C20−C70 (500−600 °C)	>C70 (>600 °C)
	Gas/naptha (wt %)	Gasoline (wt %)	Kerosene (wt %)	Diesel oils (wt %)	Lubricating oils (wt %)	Fuel oils (wt %)	Residue (wt %)
Ng, 400 °C	0.12	1.45	6.05	25.23	54.3	0.71	12.12
Ng+PS	0.12	1.09	3.69	12.95	76.7	0.42	5.02

than that of the Ng 300 °C, which indicates a lower dispersity in the Ng+PC crude oil components. This could support that Ng+PC crude oil mainly contains aromatic compounds and has a simpler composition. The molar mass distribution of Ng+PS crude oil has a similar shape and range when compared to Ng 400 °C crude oil, confirming that they share minor differences, which is in line with the result of the elemental analysis, FTIR, and ^{1}H NMR. Above all, the major constitutes in the Ng+PC crude oil are aromatic compounds, which could be used as an intermediate product to obtain aromatic chemicals. The addition of PS generates more crude oil with slight changes of properties; therefore, the Ng+PS crude oil is suggested for use in biofuel applications.

3.3.4. Gas Chromatography Mass Spectrometry Analysis. To explore the application potential of crude oil, GC-MS analysis was conducted to reveal its chemical composition in greater detail. The major identified compounds in the pure Ng crude oil are *n*-hexadecanoic acid (7.5%), *p*-isopropenylphenol (4.9%), phenol (2.8%), phenol, 4-(1-methyl-1-phenylethyl) (2.6%), and ethyl 4-oxo-2-phenylpentanoate (6.7%), while the area of the compounds which can be identified by GCMS was only 20% of the total area. As shown in Figure 9, the total ion chromatograms of Ng+PC crude oil have much simpler patterns than the Ng 300 °C crude oil, and the major peaks are identified as listed in Table 8. It can be confirmed that *p*-isopropenylphenol, phenol, and phenol, 4-(1-methyl-1-phenylethyl) are the major compounds in the Ng+PC crude oil. They are mainly the monomers of PC plastic, which are important intermediates in the production of stabilizers and dyestuff production.[35] The differences between Ng+PS and Ng 400 °C crude oil occur mostly within the retention time range from 18 to 21 min; the major compounds are also listed in Table 8. With the addition of PS, crude oil consists of more aromatic hydrocarbons with less oxygen atoms, which are highly flammable and often used for motor fuels such as gasoline or diesel. Thus, PS can be used as an additive in the microalgae HTL to improve crude oil yield and quality.

3.3.5. Thermogravimetric Analysis. TGA analysis measures the mass loss at a programmed temperature, which is reported to be a simple tool to determine the molecular weight and the length of the carbon chain of oil sample; it then can be attributed to different coke oil type groups (Handbook of Petroleum Product analysis, JG Speight, 2008).[36] As Ng+PS crude oil is considered to be more suitable for biofuel application, a TGA analysis was performed to determine the oil type distribution of Ng 400 °C and Ng+PS samples. As shown in Table 9, the major constituents in both crude oil samples are the compounds with the same boiling point ranges of diesel oils (170−250 °C) and lubricating oils (250−500 °C), which in total make up up to 80 wt %. The addition of PS shifts the oil distribution toward the lubricating oils area. In fact, it is known that the polymers are used as additives to improve the

flow properties of lubricating oil;[37] however, the physical property changes of crude oil still require further study.

■ CONCLUSIONS

The co-HTL processes of the microalgae *Chlorella vulgaris* and *Nannochloropsis gaditana* with a range of plastics were investigated in this work. The results show that *Nannochloropsis gaditana* has a better interaction ability with plastics than *Chlorella vulgaris*, which could be attributed to its higher carbohydrate content. Among the nine types of plastics tested, PS and PC exhibit the greatest potential (significantly improved crude oil yield and high synergistic effect) in the co-HTL process. Data analysis with the response surface method revealed that the process parameters follow different trends for the different materials, and equations for crude oil have been developed by conducting further response surface methodology experiments. The optimal conditions interpolated from the evaluation tool could be verified with the experiments. Ng+PC could produce a high crude oil yield of 67.2 wt % with a significant synergistic effect of +50.5% at optimal HTL conditions, and the crude oil product was found to be rich in aromatic compounds, which could be further used in the production of polymers, insecticides, and dyes. Ng+PS produced around 51.4 wt % crude oil with a slight synergistic effect of +5.6%; hence, the crude oil is suggested to be used in biofuel applications. Our findings provide a promising approach for microalgae crude oil yield improvement and effective transformation of plastic wastes into potential valued products. In future research, greater focus could be placed on the technical and practical feasibility of this technology in real-life production, for example, in order to understand the co-HTL mechanism of plastic mixtures and microalgae, as real plastic material can be blends containing additional substances (fillers, modifiers), and the effect of plastic particle size on the suitability for a continuous HTL system should be also considered. Considering that the final target of this process is to apply real plastic wastes to produce valuables, the plastic wastes would bring much impurities; therefore, a post-treatment is supposedly required.

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Notes

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