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One-pot production of hydrocarbon oil from poly (3-hydroxybutyrate)

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Abstract

Poly (3-hydroxybutyrate) (PHB) is an energy storage material of many microbial species, and is found an effective feedstock for production of renewable hydrocarbon oils. A high oil yield (up to 38.2 wt%) was obtained in a phosphoric acid (H_3PO_4) solution at mild temperatures (165-240 ^oC). PHB and crotonic acid ($C_4H_6O_2$), a dominant thermal degradation product of PHB, were deoxygenated mainly via decarboxylation, generating similar liquid and gaseous products. Carbon dioxide and propylene were the major products in gas phase with little CO formation. The hydrocarbon oil (C4-C16) is a mixture of alkanes, alkenes, benzenes and naphthalenes. Aromatics (C10-C15) were the major hydrocarbons in a 100 wt% H_3PO_4 solution, while alkenes and alkanes (C4-C9) were favored in diluted solutions (50 wt% to 85 wt% H_3PO_4). The concentration of H_3PO_4 was a key factor that affected the oil composition and yield. A high efficient decarboxylation of crotonic acid at 220 ^oC for 3 hours resulted in 70.8 wt% of oxygen being removed as CO_2 and 57.0 wt% of carbon being recovered as hydrocarbon oil. The H_3PO_4 solution can be repeatedly used for high yield oil production. This work shows that a type of new biological feedstock can be used to produce renewable hydrocarbon oil in an efficient one-pot reaction.

1 Introduction

Poly(3-hydroxybutyrate) (PHB) is a biopolyester produced by many bacterial species as an energy storage material.[1-3] It has been produced at large scales through industrial fermentation of renewable carbohydrates.[4,5] PHB is an environmentally friendly bioplastic and has the similar material properties of polypropylene for a variety of applications.[6-8] PHB is also an energy-rich polymer and, similar to bio-oil, may be a renewable feedstock for production of liquid hydrocarbons. Little work, however, has been done to convert PHB into hydrocarbons as a "drop in" transportation fuel. Crotonic acid (trans-2 butenoic acid) is the major monomeric product formed from thermal degradation of PHB[9,10]. Because of the presence of carboxyl groups, PHB deoxygenation is necessary in order to produce hydrocarbons. It has been reported that at high temperatures (>300 ^{o}C) propylene is formed from PHB decarboxylation in hydrothermal reforming[11]. Lewis-acid may play a catalytic role in decarboxylation of unsaturated carboxylic acids at high temperature (365 ^{o}C)[12]. In general, hydrotreating and thermal (catalytic) pyrolysis are two of the most studied processes for deoxygenation of carboxylic compounds in biomass. Hydrotreating under high pressure hydrogen is a typical method to obtain hydrocarbons from bio-oils, but consumes a large amount of hydrogen[13,14]. Thermal (catalytic) pyrolysis is an alternative processes for decarboxylation/decarbonylation of organic acids, which is usually performed at high temperatures (e.g., $\geq$ 300 ^{o}C)[14-19]. Thermogravimetric analysis has shown complete gasification of PHB at high temperatures (> 280 ^{o}C)[9,20,21], which implies that multiple catalytic reactors are needed to produce liquid hydrocarbons from a solid PHB-containing feedstock. Due to the worldwide demand for bio-based "drop in" transportation fuels, new renewable feedstocks such as PHB and processing technology should be explored. Specifically, a novel method for PHB deoxygenation at low temperature without hydrogen is meaningful.

Phosphoric acid (H_3PO_4) is usually considered as an indecomposable, non-volatile, non-oxidizing, mild acid, and has been used as a catalyst or solvent in many applications[22-26]. In this work, we used H_3PO_4 solution in one-pot conversion of PHB into liquid hydrocarbon oil. It is first time demonstrated that a high oil yield is achieved at relatively low temperatures (165 to 240 ^{o}C) in the absence of hydrogen.

2 Experimental section

2.1 Materials

Crotonic acid (98 wt%) and polyphosphoric acid (115 % H_3PO_4 basis) were purchased from Sigma-Aldrich (St Louis, MO, USA). Pre-determined concentrations (50 wt% to 100 wt%) of H_3PO_4 were prepared from polyphosphoric acid and distilled de-ionized water. Poly(3-hydroxybutyrate) (PHB 98 wt%) was obtained from Bio-on (Bologna, Italy). Its weight-average molecular weight (138,000 Da) and number-average molecular weight (53,100 Da) were measured with gel permeation chromatography (GPC) and calibrated with polystyrene standards. The polystyrene standards with narrow molecular weight distribution were purchased from Sigma-Aldrich.

2.2 Formation and analysis of hydrocarbon oil

In a typical experiment, 0.5 g PHB or crotonic acid and 10 mL of H_3PO_4 solution were put into a 20 mL polytetrafluoroethylene (PTFE) reactor, and the reactor was purged with N_2 for about 10 minutes. The PTFE reactor was then sealed and left for a predetermined reaction time in a thermostat oven that was maintained at a desired temperature (165 to 240 ^{o}C). After reaction, the

PTFE reactor was quickly cooled down in tap water. The reaction solution consisted of a top layer of oil products and a bottom layer of aqueous phosphoric acid solution. The oil was recovered by extraction with methylene chloride, and the water moisture of solvent solution was removed with anhydrous magnesium sulfate. After evaporation of methylene chloride at 40 ^{o}C, the oil was weighted to calculate the yield from the initial amount of PHB or crotonic acid, excluding the residual crotonic acid. During the evaporation of methylene chloride in the extracted oil samples, a control of pure methylene chloride with the same volume was put in the same condition at the same time. After the pure methylene chloride was completely evaporated, the extracted oil samples was kept in the evaporation condition for a little longer time (1-2 minutes) to make sure that the solvent methylene chloride was also completely evaporated. Duplicates or triplicates were performed to get an average yield and error range. In the experiment of phosphoric acid reuse, fresh PHB was added into the used H_3PO_4 solution to conduct the reaction under the same conditions as described above.

In order to determine the residual crotonic acid after reaction, the methylene chloride solution and the H_3PO_4 solution after solvent extraction were analyzed by using a gas chromatograph equipped with a flame ionization detector (GC-FID, Bruker 450-GC, CA, USA) and a high performance liquid chromatograph (HPLC, Shimazu, Japan), respectively. The oil products in methylene chloride were analyzed with a gas chromatograph-mass spectrometer (GC-MS, Bruker 436-GC, CA, USA), a Fourier transform infrared spectrophotometer (FT-IR, Avatar 370, ThermoNicolet, FL, USA), and a carbon-13 nuclear magnetic resonance spectrometer (^{13}C-NMR, Varian Unity Inova 400 MHz), respectively. Deuterated chloroform was used as the solvent in ^{13}C-NMR analysis. The residual chemicals left in the H_3PO_4 solution before and after extraction were also analyzed with FT-IR, and phosphorus-31 nuclear magnetic resonance spectroscopy

(^{31}P-NMR, Varian Unity Inova 500 MHz), and a total organic carbon (TOC) analyzer. The TOC results were used for carbon recovery analysis along with the determination of major gas products as shown below.

2.3 Gas formation and analysis

In a typical experiment, 3.6 g of PHB or crotonic acid and 72 mL of H_3PO_4 solution were added into a 180 mL pyro-beaker, which was put in a 600 mL autoclave (Parr Instrument, IL, USA). The autoclave was then purged with nitrogen at least ten times of the reactor volume to remove air. The reactor was sealed and heated to a pre-determined temperature. When the temperature reached the setting value in about half an hour, the reaction time was set as zero, and thereafter recorded. After reaction, the reactor was cooled down in ambient conditions and gas samples were taken by using a FT-IR gas cell for qualitative analysis. The quantitative determination of CO_2 and propylene was performed by using a gas chromatograph equipped with a thermal conductivity detector (GC-TCD, Bruker 450-GC, FL, USA) and a Carboxen-1006 Plot (30 m×0.53 mm) column. Both CO_2 and propylene were calibrated with pure gases against helium.

3 Results and discussion

3.1 Oil products analysis

The PHB- and crotonic acid- derived oils produced in typical reaction conditions (100 wt% H_3PO_4, 220 ^{o}C, 3 hours) were analyzed by ^{13}C-NMR (Fig. 1), FT-IR (Fig. 2), and GC-MS (Fig. 3), respectively. The analysis indicates that the oil products derived from both crotonic acid and PHB are almost the same. Comparing the ^{13}C-NMR spectra of the raw materials (crotonic acid and PHB) with that of their oil products indicates that the carboxyl groups were almost completely removed (Fig. 1), and aromatic, alkene and alkane groups were formed in the oil products. This is confirmed with FTIR analysis (Fig. 2). The huge absorption peak of C=O at 1700 cm^{-1} for crotonic acid and 1720 cm^{-1} for PHB disappeared in the oil products. The peaks (3100 to 2800 cm^{-1}, 1458 cm^{-1}, 1380 cm^{-1}, and 870 cm^{-1}) of oil products indicate the presence of methyl, methylene, and aromatic groups as the major groups. There is a very small peak around 1710 cm^{-1} in the FT-IR spectra of both crotonic acid and PHB derived oils, which may come from some aldehyde and/or ketone compounds. With the GC-MS analysis, a few aldehydes and ketones (e.g., retention time of 28.318 and 30.614, in Fig. 3) were detected. The GC-MS analysis also confirms that the carboxylic group of organic acid and ester were almost completely removed, and aromatics are the main products. These analytical results consistently indicate that PHB was to a great extent deoxygenated at a quite low temperature (220 ^{o}C) with formation of various hydrocarbons in one pot reaction in the absence of hydrogen. Compared with the conventional deoxygenation methods (e.g., pyrolysis and hydrotreating), this reaction system has some unique advantages in low reaction temperature and absence of hydrogen. Because of the same products formed from both PHB and crotonic acid, crotonic acid may be the key intermediate of PHB decarboxylation.

3.2 Gaseous products and analysis

The gas products formed from PHB and crotonic acid deoxygenation were analyzed with FT-IR (Fig. 4). In comparison with FT-IR spectra of pure CO_2, CO and propylene (Fig. S1, in Electronic Supplementary Information (ESI)), it was found that CO_2 was the major gas product followed by propylene, with negligible amount of CO. In another words, PHB was deoxygenated primarily via decarboxylation (CO_2), instead of decarbonylation (CO). Based on complete decarboxylation of a PHB monomer or crotonic acid ($C_4H_6O_2 \rightarrow C_3H_6 + CO_2$), the theoretical yield of CO_2 is 51.2 wt% of initial PHB. Actually, the detected CO_2 in gas phase accounts for 35.3 wt%, or 68.9 % of maximum yield. It implies that at least 68.9 % of oxygen in PHB was removed by decarboxylation. Some of oxygen might be removed by formation of water as discussed later. Similarly for crotonic acid, 70.8 % of oxygen was removed as CO_2 via decarboxylation. Along with decarboxylation, propylene was the major gaseous hydrocarbon formed from PHB or crotonic acid. A small amount of alkyl gases might also be formed, as indicated by the peaks at 3100, 2790, 1670, 1450, 910 cm^{-1} in Fig. 4 and in comparison with pure propylene in Fig. S1(in ESI). Interestingly, the FT-IR analysis also indicates that crotonic acid and PHB have almost the same gas products (Fig. 4).

3.3 Carbon recovery analysis

Since crotonic acid is the key intermediate of PHB decarboxylation and generates the very similar liquid and gas products, we used crotonic acid as the control reactant for carbon balance analysis of the reaction system. As shown in Table 1, the total carbon recovery from the initial carbon of crotonic acid was more than 90.9 wt%, which included CO_2 (18.0 wt%) and propylene (4.9 wt%) in the gas phase, hydrocarbon oil (57.0 wt%) and organic carbon residues (11.0 wt%) in the liquid phase. Very little carbon (<2.1 wt%) was formed as char in solid phase. In addition to the loss of solid carbon, a small amount of carbon in the gas phase such as alkyl is also not included in the carbon balance, even though they were detected by FT-IR (Fig. 4). Compared with many biomass-to-liquid researches where only 25-45 % of initial carbon was recovered[27], this research has a quite good carbon recovery. Importantly, the hydrocarbon oil contains 57.0 wt% of initial carbon, which is miscible with methylene chloride and hexane (data not shown here).

3.4 Effect of H_3PO_4 concentration

Phosphoric acid is the catalyst in decarboxylation of PHB, and its concentration has a significant effect on PHB conversion and oil yield in typical reaction conditions (220 ^{o}C, 3 hours) as shown in Fig. 5. Crotonic acid was a major intermediate of PHB reaction in 50 wt% H_3PO_4. With increase of H_3PO_4 concentration, the residual crotonic acid content decreased, and little crotonic acid was remained in the 100 wt% H_3PO_4 and polyphosphoric acid (115% H_3PO_4 basis). The PHB-derived oil yield increased from 5.4 wt% to 37.3 wt% correspondingly with the increase of H_3PO_4 concentration from 50 wt% to 100 wt%. Little char (<2 wt%) was formed in these H_3PO_4 solutions. In polyphosphoric acid solution, however, a substantial amount of char (55.5 wt%) was formed, and the oil yield declined to 5.2 wt% of initial PHB. Carbonization of PHB or its derived hydrocarbons became the predominant reaction in polyphosphoric acid solution. A similar effect of phosphoric acid on crotonic acid was also observed and showed in Fig. 5. We suspect that PHB carbonization occurs after its thermal degradation into crotonic acid. This fact also supports our previous conclusion that crotonic acid is the key intermediate of PHB conversion into hydrocarbon oil.

The concentration of H_3PO_4 also affected the composition of the PHB-derived oils as revealed by their GC-MS chromatograms (Fig.3 and Fig.S2 in ESI). Table 2 gives the relative peak area (%) of the chemicals identified by GC-MS analysis. Specifically, aromatics (benzene and naphthalene derivatives) were the main oil products in 100 wt% H_3PO_4, and the naphthalene derivatives via ring condensation[28] predominated in polyphophoric acid solution. Formation of high C/H ratio hydrocarbons in high phosphoric acid is in agreement with our previous observation on char formation in polyphosphoric acid. A few unsaturated ketones and aldehydes were detected by GC-MS analysis, which may be produced together with CO_2 and water by phosphoric acid catalytic deoxygenation of PHB/crotonic acid in considering of former reports[16,29,30]. Furthermore, the existence of unsaturated ketones and aldehydes implies a possible way for aromatics formation, which may occur by some transient intermediate ketones and aldehydes through acid catalytic aldol condensation, dehydration and aromatization reactions[31-33]. In diluted phosphoric acid solutions (70-85 wt%), however, acyclic alkenes and alkanes or cyclo-alkenes and alkanes became the important oil compounds, which means aromatization reactions should be somewhat inhibited. In 50 wt% H_3PO_4, the O-containing compounds were the main products, indicating that PHB deoxygenation was not completed yet. For conclusion, phosphoric acid concentration is a potential tool in controlling oil yield, deoxygen extent, and the hydrocarbon composition.

Furthermore, high concentration of H_3PO_4 was favorable to formation of hydrocarbons with high carbon numbers (Table 3). C4-C9 compounds were the main products in 50 wt% H_3PO_4 solution while C10-C15 became the main products in 100 wt% H_3PO_4 solution. Based on the carbon numbers and the content of aromatics [34], the oil produced in 100 wt% H_3PO_4 could be a 'drop in' gasoline. According to the residual crotonic acid content, oil yield and product distribution, 100 wt%H_3PO_4 is an interesting catalyst solution for PHB deoxygenation. We further investigated the influence of reaction time and temperature on PHB conversion and oil yield.

3.5 Effect of reaction temperature and time

Temperature had apparent effect on residual crotonic acid content and oil yield from 165 to 220 ^{o}C in both PHB and crotonic acid reactions (Fig. 6). The residual crotonic acid content decreased while the oil yields increased with the increase of temperature. Little residual crotonic acid was detected at 220 ^{o}C or above, indicating that this mild temperature is high enough for complete conversion of PHB and crotonic acid. The highest oil yield (38.2 wt%) of PHB was obtained at 230 °C, and further increase of temperature didn't result in higher oil yield. This oil yield is very high, compared with the highest hydrocarbon oil yield (17.78 wt%) from catalytic co-deoxy-liquefaction of biomass and vegetable oil at 350–500 °C[35]. Besides, the reaction temperature is also much lower than those of conventional biomass deoxygenation. Interestingly, the PHB derived oils produced at different temperatures have very similar peak distribution in their GC-MS chromatograms (Fig. S3, in ESI). This fact indicates that temperature is not an important factor in determining the oil composition.

The influence of reaction time on PHB conversion was tested in 100 wt% H_3PO_4 at 220 °C (Fig. 7). Three hours seemed sufficient for complete conversion of PHB, as little crotonic acid was detected in both PHB and crotonic acid reactions. Extension of reaction time (e.g., 6 or 9 hours) seems not beneficial, because the yield of PHB-derived oil declined to some extent with extended reaction time. Some products such as char which are not soluble in methylene chloride were formed in extended reaction. As mentioned in the method of oil recovery, the insoluble products are not accounted for hydrocarbon oil. On the other hand, the influence of reaction time on PHB conversion showed quite similar results of crotonic acid conversion, which implies again that crotonic acid is the key intermediate of hydrocarbon oil production.

3.6 Reuse of H_3PO_4 solution

As shown in Fig. 8, the PHB-derived oil yield in a 100 wt% H_3PO_4 was consistently higher than 32% in repeated use for 6 times. We compared the FT-IR spectra of the fresh and used acid solution (Fig, S4 in ESI), and found no visible change. We also compared the P-NMR spectra of the acid solutions (Fig.S5, in ESI) and found that $H_4P_2O_7$ in fresh acid solution disappeared in the reused acid solutions. Most likely, A self-dissociation reaction of $H_4P_2O_7$ occurred in the solution ($2H_3PO_4 \leftrightarrows H_4P_2O_7+H_2O$)[25,36,37] and the water was provided from PHB deoxygenation.

In another words, some oxygen was removed as H_2O, forming high C/H hydrocarbons or even char. We also demonstrated that oil yield declined in diluted acid solutions. This may explain why the oil yield declines a little bit with water formation in the reused acid solution.

3.7 Reaction mechanism

As shown above, crotonic acid is the key intermediate in conversion of PHB into hydrocarbon oil. Research on PHB thermal degradation has revealed that two neighboring monomeric units of a PHB backbone form a transient structure of a six-member ring, resulting in one unsaturated end and one carboxylic acid end [38,39]. Sequential or simultaneous degradation of the oligomers finally generates crotonic acid. It is widely accepted that this transient structure occurs predominantly in thermal degradation of PHB, particularly at the melting point (around 180 ^{o}C) or above because the PHB backbone has a great flexibility to form the planar six-membered ring structure.

Decarboxylation of crotonic acid ($C_4H_6O_4 \rightarrow CO_2 + C_3H_6$) occurs because of conjugation of the unsaturated bond (-C=C-) and the carboxy bond (C=O). The promotion effect of the conjugation effect is confirmed when butanoic acid, a saturated C4 acid, was treated in the same conditions, but generating little deoxygenated products (data not shown here). Obviously, propylene is formed along with decarboxylation of crotonic acid. We originally believed that propylene undergoes radical oligomerization to generate a complex mixture of hydrocarbons (>C6). However, when propylene was used as a gas reactant, the hydrocarbons formed were not identical with those formed from crotonic acid and PHB (Fig. 3). Specifically, we observed two major products derived from both crotonic acid and PHB and their retention times in GC-MS chromatograms are 32.520 min and 41.909 min, respectively. They are tentatively identified as a 1,2,3,4-tetramethyl-5-(1-methylethyl)- benzene and a 3,3,4,5,7-pentamethyl-1-indanone based on their high match probability (≥ 890 ‰) of MS spectra (Fig. 3). The lack of these two major products from propylene reaction implies that propylene is not a key intermediate but a byproduct of deoxygenation of crotonic acid and PHB. A very active intermediate might be formed in decarboxylation of crotonic acid, and hydrocarbons could be formed directly from the intermediate rather than from propylene. It should be pointed out that propylene can also be converted into hydrocarbon products with phosphoric acid catalysts[24,40-42]. Further investigation is needed on the reaction mechanism, especially on what happens after crotonic acid is formed from PHB degradation.

4 Conclusions

PHB is a type of new renewable feedstock from which hydrocarbon oil is effectively produced in a simple one-pot reaction. Compared to conventional biomass processing, PHB processing demonstrated in this work has some technical advantages such as mild reaction temperature (around 220 ^{o}C), cheap reusable catalyst (80-100 wt% H_3PO_4), and high oil yield (38.2 wt%) without using hydrogen.

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Notes and references

Electronic Supplementary Information (ESI) available: FT-IR spectra of CO_2, CO, propylene, and various status of H_3PO_4 solution; GC-MS analysis of PHB derived oils produced at various H_3PO_4 concentrations and temperatures; ^{31}P-NMR analysis of fresh 100 wt% H_3PO_4 and the H_3PO_4 solution after reaction.

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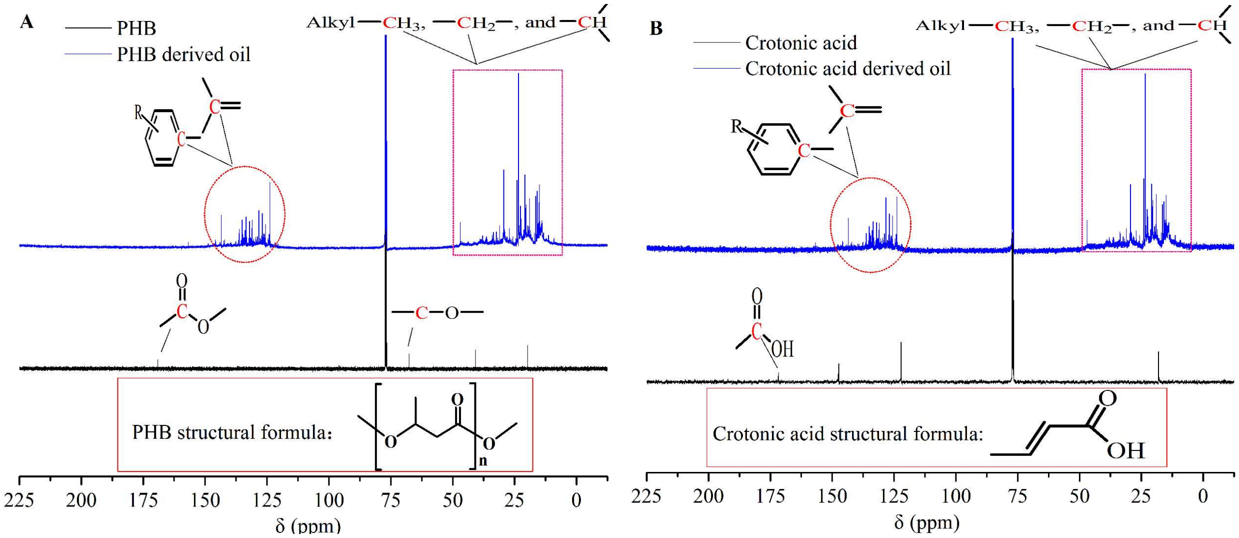

Fig. 1. ^{13}C-NMR spectra of PHB, crotonic acid and their oils produced in 100 wt% H_3PO_4 at 220 °C for 3 hours.

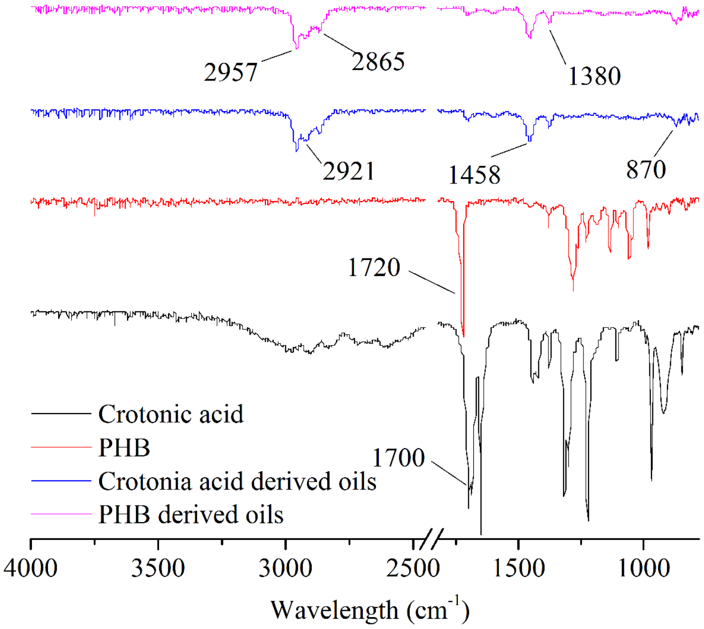

Fig. 2. FT-IR spectra of PHB, crotonic acid and their oils produced in 100 wt% H_3PO_4 at 220 ^{o}C for 3 hours.

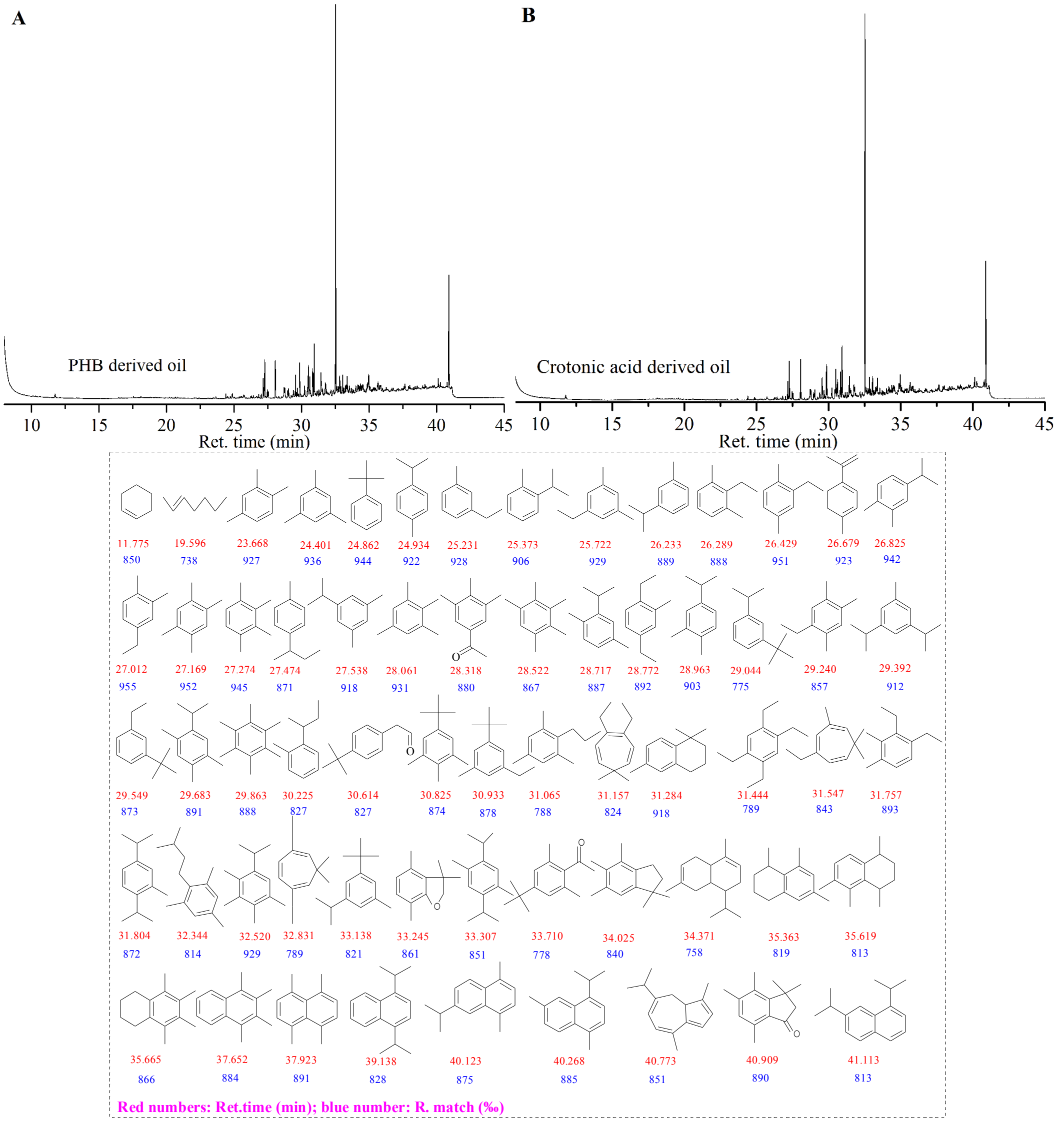

Fig. 3. GC-MS analysis of PHB- and crotonic acid-derived oils produced in 100 wt% H_3PO_4 at 220 ^{o}C for 3 hours.

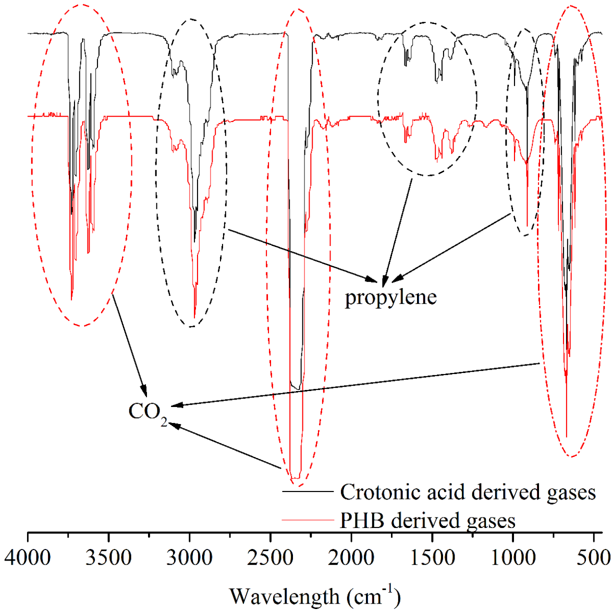

Fig. 4. FT-IR spectra of PHB- and crotonic acid-derived gases.

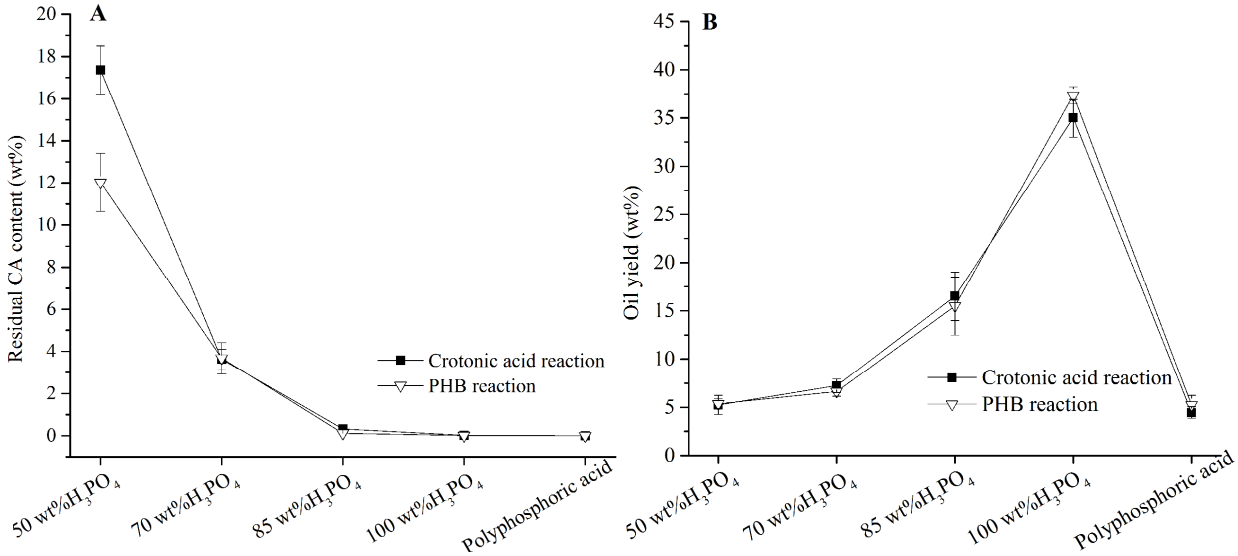

Fig. 5. The effect of H_3PO_4 concentration on residual crotonic acid content and oil yield at 220 ^oC for 3 hours.

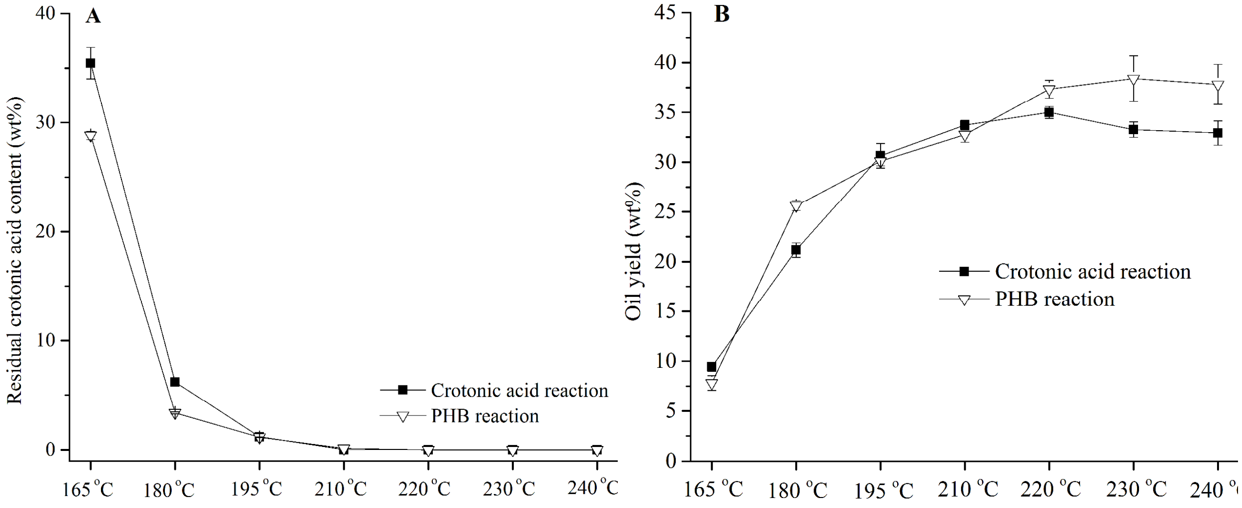

Fig. 6. The effect of reaction temperature on residual crotonic acid content and oil yield in 100 wt% H_3PO_4 for 3 hours.

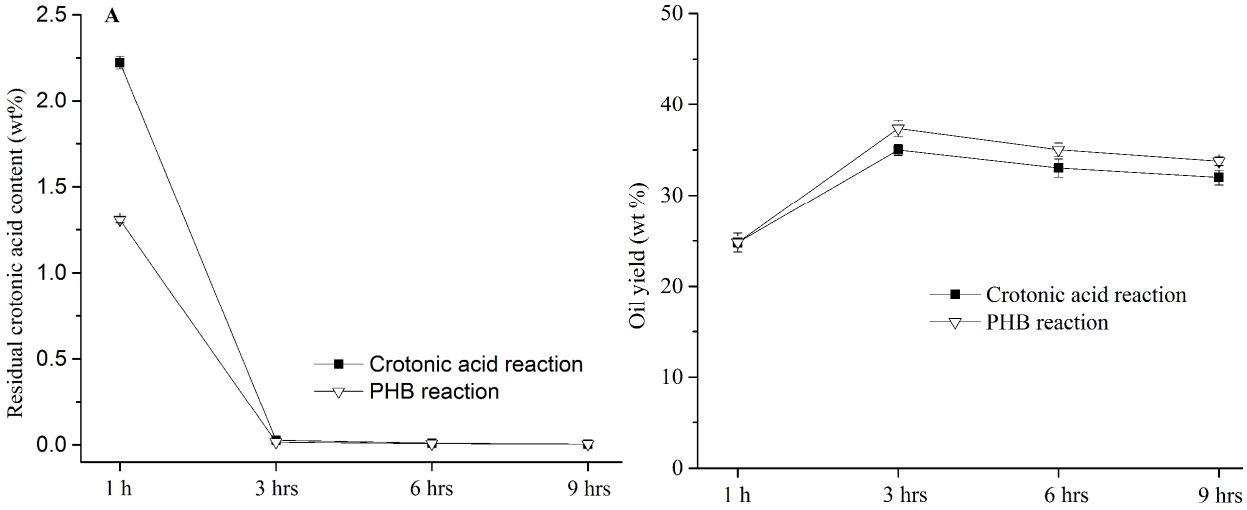

Fig. 7. The effect of reaction time on residual crotonic acid content and oil yield in 100 wt% at 220 ^{o}C.

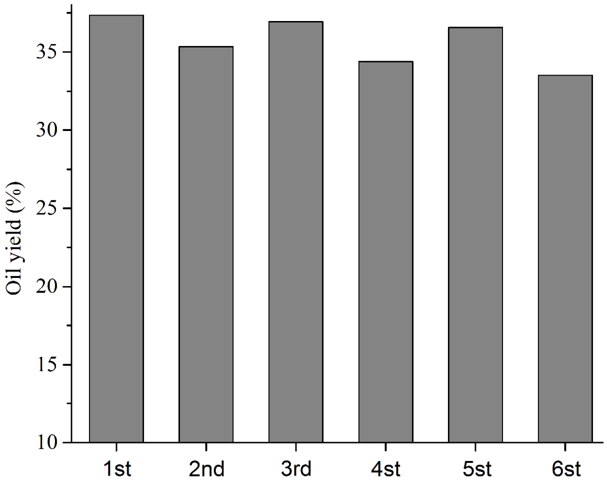

Fig. 8. The yield of PHB-derived hydrocarbon oil in a reused H_3PO_4 (100 wt%) solution at 220 ^oC for 3 hours.

Table 1. Carbon recovery of crotonic acid decarboxylation and oil formation.[a]

Phase	Products	Carbon recovery (wt%)[b]
Gas	CO_2	18.0
	C_3H_6	4.9
Liquid	Oil	57.0
	Residues in H_3PO_4 solution[c]	11.0
Solid	Char	$<$2.1%[d]
	Total	>90.9%

Note: *a,* The reaction was performed in 100 wt% H_3PO_4 solution at 220 °C for 3 hours; *b*, the carbon mass percentage recovered from the initial carbon of crotonic acid; *c*, the residual organic carbons left in H_3PO_4 solution; *d*, the carbon content of char is assumed 60 wt%.

Table 2. Chemical distribution of PHB-derived oils generated in different phosphoric acid solutions at 220 °C for 3 hours

	Relative peak area (%)						
	O-containing compounds	Acyclic alkanes	Cycloalkanes	Acyclic alkenes	Cycloalkenes	Benzenes	Naphthalenes
50 wt% H_3PO_4	66.3	3.7	1.6	16.7	3.9	7.7	0
70 wt% H_3PO_4	27.5	1.7	1.0	61.7	3.8	4.3	0
85 wt% H_3PO_4	16.2	3.2	3.7	57.1	1.7	18.1	0
100 wt% H_3PO_4	15.2	0.7	0.4	0.2	5.2	72.0	6.3
Polyphosphoric acid	0	0	0	0	18.4	52.6	28.9

Note: The chemical structures are identified with GC-MS

Table 3. Carbon distribution of PHB-derived oils formed in different phosphoric acid solutions at 220 °C for 3 hours.

	Relative peak area (%)												
	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13	C14	C15	C16
50 wt% H_3PO_4	12.1	4.6	5.3	31.2	5.9	24.3	2.6	0.6	4.6	8.8	0	0	0
70 wt% H_3PO_4	5.5	0	3.1	20	2.7	59.6	4.9	0	0.3	3.6	0.3	0	0
85 wt% H_3PO_4	0.8	0	0.7	4.5	5.1	34.2	21.2	6.8	8.8	13.6	1.8	2.5	0
100 wt% H_3PO_4	0	0	0.4	0	0.2	1.1	8.5	5.3	13.1	40.5	24.7	6.2	0
Polyphosphoric acid	0	0	18.4	0	0	0.2	13.6	8	10	20.9	6.2	18.0	4.7

Note: The carbon numbers distributions are based GC-MS analysis