

## Article

# Development of a Two-Stage Pyrolysis Process for the End-Of-Life Nickel Cobalt Manganese Lithium Battery Recycling from Electric Vehicles

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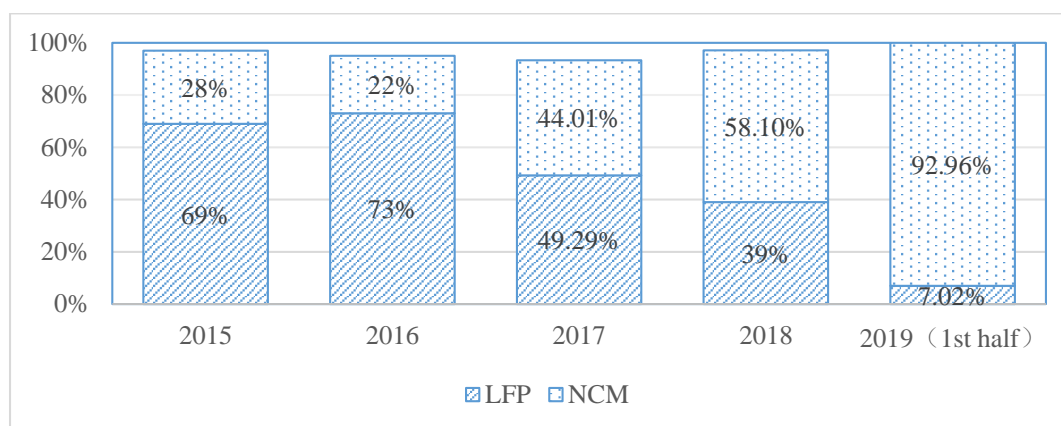


**Abstract:** With the continuous promotion of electric vehicles, the pressure to scrap vehicle batteries is increasing, especially in China, where nickel cobalt manganese lithium (NCM) batteries have gradually come to occupy a dominant position in the battery market. In this study, we propose a two-stage pyrolysis process for vehicle batteries, which aims to effectively deal with the volatilization of organic solvents, the decomposition of lithium salts in the electrolyte and the removal of the separator material and polyvinylidene fluoride (PVDF) during battery recycling. By solving these issues, recycling is more effective, safe. Through thermogravimetric analysis (TGA), the pyrolysis characteristics of the battery's internal materials are discussed, and 150 °C and 450 °C were determined as the pyrolysis temperatures of the two-stage pyrolysis process. The results show that in the first stage of pyrolysis, organic solvents EC (C<sub>4</sub>H<sub>3</sub>O<sub>3</sub>), DEC (C<sub>5</sub>H<sub>10</sub>O<sub>3</sub>) and EMC (C<sub>4</sub>H<sub>8</sub>O<sub>3</sub>) can be separated from the electrolyte. In the second stage, the pyrolysis can lead to the separator's thermal decomposition. The gas products are alkane C<sub>2</sub>–C<sub>6</sub>, and the tar products are organic hydrocarbons C<sub>15</sub>–C<sub>36</sub>. Meanwhile, the solid residue of the battery's internal material seems to be very homogeneous. Finally, the potential recovery value and pollution control countermeasures of the products and residues from the pyrolysis process are analyzed. Consequently, this method can effectively handle NCM vehicle battery recycling, which provides the basis for the subsequent hydrometallurgical or pyrometallurgical process for element recovery of the battery material.

**Keywords:** vehicle battery; pyrolysis; NCM battery; recycling; EOL; TGA; GC/MS; ICP

## 1. Introduction

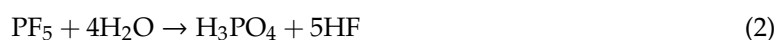
With the intensification of environmental and resource issues, the electric vehicle (EV) as one of the most important countermeasures, has been gradually developing globally. Since 2015, China's EV annual sales have been the highest in the world [1]. In 2018, when global EV annual sales historically exceeded 2 million, China contributed 1.25 million of them, which occupied over 4.4% of the new car sales market [2]. In China, the electric vehicle battery market has mainly used lithium iron phosphate batteries (LFP) and nickel cobalt manganese lithium batteries (NCM), as shown in Figure 1 [2–9]. The proportion of the NCM battery market has been increasing in recent years and has become dominant. It is estimated that by 2020, the total domestic demand for lithium batteries will be 153 GWh, and the corresponding demand for electrolyte will reach 227,000 tons [3]. It is predicted that the amount of scrap vehicle batteries will reach 120–170 thousand tons [10] in 2020 and 11.36 million tons in 2030 [11]. According to the composition of the Li-ion battery [12], waste electrolytes will reach 1.33–1.61 million tons in China in 2030, which may be dangerous and result in environmental issues.



**Figure 1.** The annual proportion of electric vehicle (EV) battery types in the Chinese market [2–9]. LFP: lithium iron phosphate batteries; NCM: nickel cobalt manganese lithium.

In recent years, research on spent Li-ion battery (LIB) recycling has become a hotspot in the world, and recycling processes are often focused on the recycling of cobalt and nickel [13]. In particular, the ternary battery NCM contains heavy metals (such as Co and Ni) with recycling value according to the price statistics from the Shanghai Metals Market [12,14–17]. The main steps of used battery recycling are pretreatment, pyrometallurgy and hydrometallurgy methods [16,18]. Recovery of metals such as Co, Ni, Li, Al, Cu is the primary recycling target in these studies, and the recycling rate and product quality are at a high level, especially by the hydrometallurgy method [19–22], while the pyrometallurgy method ignores the recovery of lithium [23,24]. Of course, combining pyrometallurgy with hydrometallurgy can improve both the recycling efficiency and recycling rate [25]. Regarding the pretreatment process, the methods are commonly discharge, dismantling, crushing and physical separation, which are often the prerequisite for the subsequent stages [18].

On the other hand, the electrolyte of a vehicle battery often contains organic solvents and lithium salts (such as  $\text{LiPF}_6$ ). The organic solvents usually consist of carbonates, as shown in Table 1, which may lead to burning because of the low flash point. Meanwhile, the hazard of fluoride generated by the decomposition of lithium salts, shown as below in Equations (1) and (2), should be regarded as an important safety and environmental issue [26–29]. Therefore, the recycling of used NCM EV batteries has economic value and environmental protection significance.



**Table 1.** Flashpoint of organic solvents commonly used in vehicle batteries.

Organic Solvent	DMC ( $\text{C}_2\text{H}_6\text{O}_2$ )	DEC ( $\text{C}_5\text{H}_{10}\text{O}_2$ )	EC ( $\text{C}_3\text{H}_4\text{O}_3$ )	EMC ( $\text{C}_4\text{H}_8\text{O}_3$ )
Flash/boiling point	18 °C/89 °C	33 °C/126 °C	157 °C/248 °C	23 °C/109 °C

So far, China has promulgated a series of policies and standards such as Chinese national recommended standard (GBT) for the recycling and management of vehicle batteries, as shown in Table 2. The content mainly covers the aspects of recycling responsibility regulation, recycling network establishment, recycling rate requirement for valuable metals such as Ni and Co, dismantling and cascade use specifications. However, there are no specific requirements, and treatment methods are given for the treatment of the vehicle battery's electrolytes, separator, etc. In terms of pretreatment and safe handling of electrolytes, TOXCO Inc.'s process was to freeze waste batteries in liquid nitrogen at a low temperature before crushing [25,26,28], but it still cannot avoid lithium salt decomposition

and organic solvent volatilization during subsequent processing. In the battery disassembly and crushing process, Recupyl [28] produced an inert atmosphere of argon and carbon dioxide to protect the environment, but once the subsequent process is exposed to the air, it will also cause dangers by fluoride and organic solvents. Consequently, it is far from enough to use usual pretreatment methods such as discharge and mechanical crushing for waste battery before pyrometallurgy or hydrometallurgy.

**Table 2.** Policies and standards related to vehicle battery recycling.

Policies [30]	Highlights
2006, Automotive product recycling technology policy	Extended producer responsibility for electric vehicle manufacturers
2012, Planning for the development of the energy-saving and new energy vehicle industry (2012–2020)	Cascade use and standards construction of waste battery
2016, Electric vehicle battery recycling technology policy	Recovery rate: Ni, Co, Mn $\geq$ 98%
2018, New energy vehicle battery recycling interim measures	Reiterate the responsibility of batteries recycling;
2018, New energy vehicle battery recycling on traceability management interim measures	Establishment of traceability platform and coding identification of battery products
2019, New energy vehicle battery recycling on service network construction and operation guide [31]	Recycling network construction
2019, Industry standard conditions of new energy vehicle used battery utilization and interim administrative measures [31]	Recovery rate: Ni, Co, Mn $\geq$ 98% by hydrometallurgy; Ni and Rare earth elements $\geq$ 97% by pyrometallurgy
Standards	Highlights
GBT 33059-2016: Methods for disposal and recycling of lithium-ion battery material wastes	Recovery rate: Cu and Al $\geq$ 90%, Ni and Co $\geq$ 99% and Mn $\geq$ 95%; The removal of binder and separator by 500–600 °C pyrolysis
GBT 33598-2017: Recycling of traction battery used in electric vehicle—dismantling specification	Waste battery dismantling specification
GBT 34013-2017: Dimension of traction battery for electric vehicles	Battery classification
GBT 34014-2017: Coding regulation for automotive traction battery	Code for battery products
GBT 34015-2017: Recycling of traction battery used in electric vehicle—test of residual capacity	Residual capacity detection method for battery

According to existing studies, pyrolysis was considered as an alternative pretreatment method for recycling spent LIBs, which can decompose the organic material such as polyvinylidene fluoride (PVDF) at a high temperature (such as 600 °C) to facilitate the separation of powdered metal oxide on aluminum foils for subsequent hydrometallurgical processes [13,32–34]. The separation of electrodes by pyrolysis is better than the binder removal by N-methylpyrrolidinone (NMP) [18], which may affect the recycling of materials and produce wastewater [32,34,35].

However, the organic solvents in electrolytes, shown in Table 1, will also evaporate during pyrolysis without receiving much attention. In fact, there is no need for high-temperature energy consumption according to these solvents' physical characteristics [25]. In addition, the organic solvents

with low flash points are not suitable for mixing with high pyrolysis products, which often include flammable small molecule gases such as alkanes.

In this study, for waste NCM batteries, a two-stage pyrolysis method was used to reduce the harm of the electrolyte in the pretreatment stage and to facilitate the recovery of subsequent process materials. Generally speaking, the research objective is to deal with the volatilization of organic solvents and electrolyte decomposition in the electrolyte at the first-stage temperature. In order to facilitate subsequent material recovery, the second-stage temperature pyrolysis will deal with the separator such as Polypropylene/polyethylene (PP/PE) and adhesive such as PVDF. Firstly, the characteristics of pyrolysis of decommissioned NCM batteries are explored by thermogravimetric analysis (TGA) to guide the pyrolysis process temperature determination. Then, the composition of pyrolysis products from two stages is analyzed using the gas chromatography-mass spectrometry (GC/MS) method. In addition, the energy recovery potential of the pyrolysis products is explored to promote resource recovery. Lastly, the pyrolysis residue is detected by an inductively coupled plasma optical (ICP) instrument to check the effectiveness of the process.

## 2. Materials and Methods

### 2.1. Materials

The waste NCM EV batteries used in this research were from a scrap car dismantling company. The batteries were produced by CATL Co., Ltd. (Fujian province, China), which occupies an important position in the global vehicle battery market. The weight of the battery was 0.83 kg with the rated voltage 3.65 V and rated capacity 146 Wh.

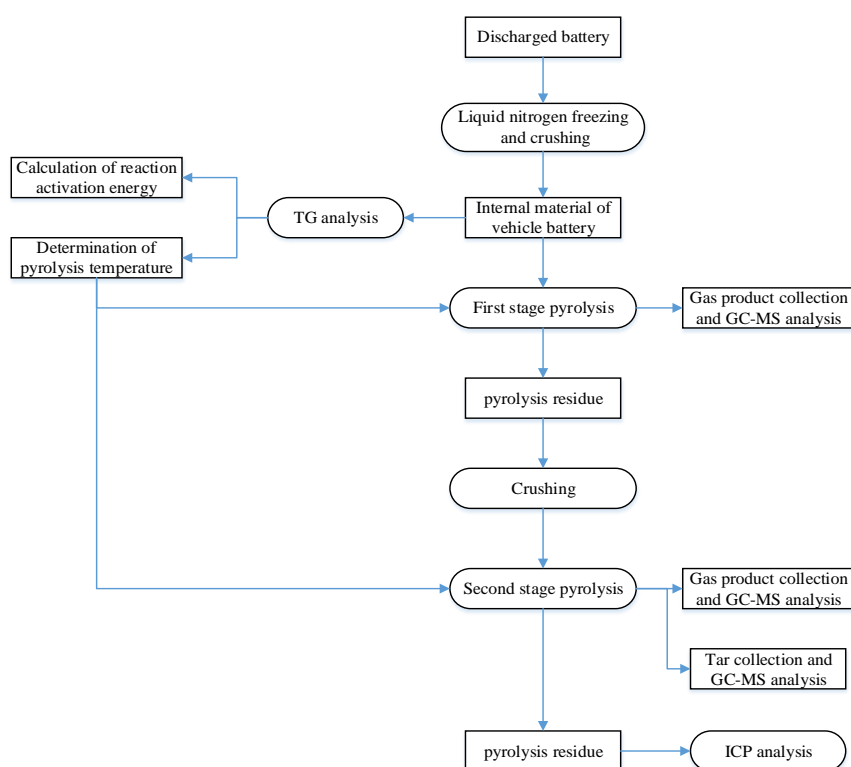
The composition and content of the battery has been provided by CATL Co., Ltd., shown in Table 3. Among them, the cathode electrode contains elements such as Ni, Co, Mn and Li, and the anode electrode uses graphite material. The electrolyte consists of lithium salt ( $\text{LiPF}_6$ ). Organic solvents are carbonate. The polyolefin such as PP/PE are used as the separator materials, and PVDF is used for the binder. The batteries have been deeply discharged by immersion in a salt water pool to make them inactive.

**Table 3.** Material composition of selected NCM battery.

Composition	Mass Ratio
Cathode material	28.2%
Anode material	18.3%
Copper	11.4%
Aluminum	19.7%
Binder	2.4%
Electrolyte	1.9%
Electrolyte solvent	10.8%
Separator	2.0%
Plastics	1.2%
Others	4.1%

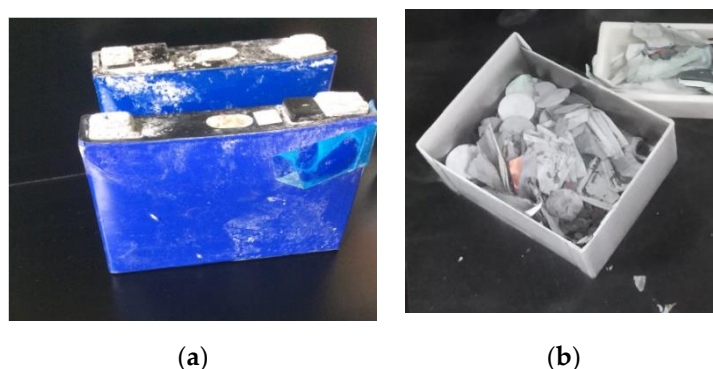
### 2.2. Experiment Process

Figure 2 shows the methodology flowchart of this research. The purpose of this study is to deal with the volatilization of organic solvents and decomposition of lithium salts in the electrolyte of NCM batteries through the first stage of pyrolysis. Then, the separator and binder are removed by the second stage of pyrolysis to provide the basis for subsequent battery material recycling. The potential value of energy recovery from the pyrolysis products are also discussed.



**Figure 2.** The methodology flowchart of two-stage pyrolysis process.

Even if a spent battery, as seen in Figure 3a, is deeply discharged, if it is directly disassembled there is still a potential danger of organic solvent burning and fluoride production. Therefore, liquid nitrogen was firstly employed to cool the battery before dismantling. After that, the material inside the vehicle battery as Figure 3b shown was separated and extracted.



**Figure 3.** (a) The waste nickel cobalt manganese lithium (NCM) battery, (b) internal materials.

Secondly, the temperature of the pyrolysis process was confirmed. As the detailed composition of the NCM battery materials was not fully known, especially the types of organic solvents, which results in ambiguity in the research. In this study, we used TGA to explore the internal materials' pyrolysis characteristics and determine the suitable temperature for pyrolysis process. From the perspective of the feasibility analysis of the pyrolysis process, the required reaction activation energy was calculated based on the pyrolysis kinetics.

Based on the results of TGA, pyrolysis was performed at the first temperature stage, and the gas product was analyzed by GC/MS analysis. The main purpose of this step is to deal with the volatilization of the organic solvent and accelerate the decomposition of the fluoride to avoid harm

caused by the fluoride. In the second stage of pyrolysis, the separator in the remaining materials is expected to be pyrolyzed and removed, and the recovery value of pyrolysis production was also explored by GC/MS analysis. Meanwhile, the coating of the electrode material by the binder (PVDF) was removed to implement the effective separation of the electrode material from other parts by the plan, so as to facilitate the subsequent metal recycling process in the future. Before the second pyrolysis stage, crushing was used to improve the pyrolysis efficiency. The elemental analysis of remaining solid residues was performed by ICP detection.

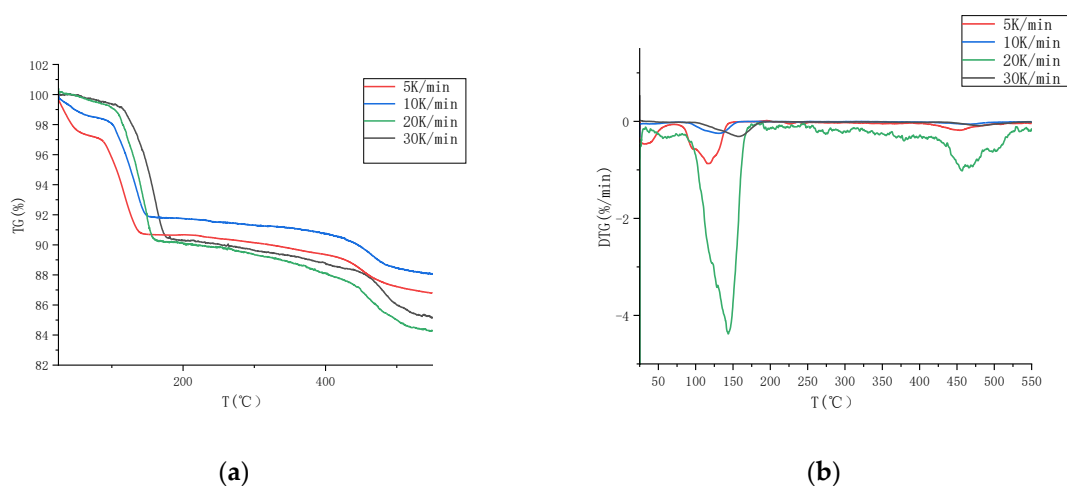
In this study, the TGA was carried out by the Pyris 1 TGA (PerkinElmer Company, Waltham, MA, USA). The GC/MS analysis for pyrolysis gas production was determined by Agilent 7890B-5977B (Santa Clara, CA, USA). The ICP detection of the solid product after pyrolysis was completed by Thermo iCAP6300 (Waltham, MA, USA). The elemental analysis isotope mass spectrometry (EAI) analysis for tar production was implemented by Elementar Vario EL III (Hanau, Germany). All the equipment was from the Instrumental Analysis Center (Instrumental Analysis Center of Shanghai Jiaotong University. <http://iac.sjtu.edu.cn/>) in Shanghai Jiaotong University.

### 3. Results and Discussion

#### 3.1. Pyrolysis Characteristics

##### 3.1.1. Determination of Pyrolysis Temperature

In order to explore the relationship between the decomposition/volatilization rate of the internal materials of the battery and the temperature, the retired NCM vehicle battery was manually broken by a cutting machine. Then, the case was removed and a small piece of the internal materials of the battery was extracted by shears for TGA, as shown in Figure 3b. In this study, TGA was performed at heating rates of 5 K/min, 10 K/min, 20 K/min and 30 K/min. The characters of pyrolysis are shown in Figure 4a,b.



**Figure 4.** (a) The TG curves, (b) the DTG curves.

According to the TG results, pyrolysis/volatilization mainly occurred in two stages, and the 20 K/min heating rate curve is the most characteristic representative. In the first stage (90–180 °C), the volatilization of organic solvents and the decomposition of lithium salts mainly occurred, and the peak of its reaction rate was around 150 °C. In the second stage (400–480 °C), thermal decomposition of the separator and PVDF occurred, and the peak of the reaction rate was at about 450 °C. Based on the analysis of the results of TG, the subsequent two-stage pyrolysis temperatures of the waste NCM batteries were determined by 150 °C and 450 °C, respectively.

### 3.1.2. Calculation of Reaction Activation Energy

Based on the results of different heating rates in this study, shown in Figure 4, pyrolysis kinetics were employed to calculate the reaction activation energy of the internal materials of the spent NCM battery to reflect the feasibility of the pyrolysis process for used battery treatment. The pyrolysis kinetics model is as follows:

$$\frac{dx}{dT} = \frac{A}{\beta} f(x) \exp\left(\frac{-E}{RT}\right) \quad (3)$$

where  $x$  is the conversion rate of the reaction substance;  $f(x)$  is the reaction mechanism function;  $T$  is the pyrolysis temperature;  $A$  is the former coefficient;  $\beta = dT/dt$  is the heating rate of pyrolysis;  $E$  is the reaction activation energy;  $R$  is the gas constant valued 8.314 J/(mol·K).

According to Ozawa's method of solving the activation energy [36] and Doyle's approximation [37], Formula (3) can be approximated as follows [38]:

$$\lg\beta = \lg\left(\frac{AE}{RG(x)}\right) - 2.315 - 0.4567 \frac{E}{RT} \quad (4)$$

$$G(x) = \int_0^x \frac{dx}{f(x)} \quad (5)$$

In Equation (4),  $\lg(AE/RG(x))$  is a constant when the conversion rate  $x$  is a determined value; thereby,  $\lg\beta$  is proportional to  $1/T$ . In this study, based on the linear regression analysis, the activation energy  $E$  can be calculated by the regression slope.

Specifically, the conversion rates were  $x = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9$ . Pyrolysis temperatures correspond to different conversion rates under different heating rates, respectively, as shown in Table 4.

**Table 4.** The temperature corresponding to the conversion rate  $x$  at different heating rates.

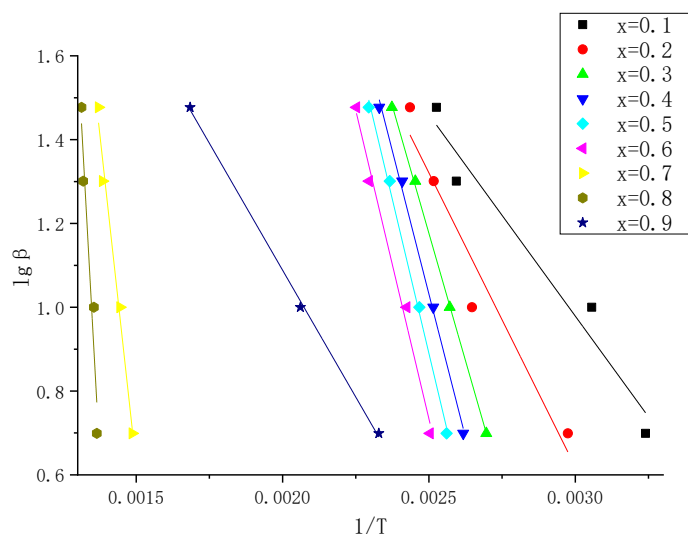
Heating Rate (K/min)	Mass Loss (wt%)	Temperature T (°C) Corresponding to Conversion Rate $x$								
		$x = 0.1$	$x = 0.2$	$x = 0.3$	$x = 0.4$	$x = 0.5$	$x = 0.6$	$x = 0.7$	$x = 0.8$	$x = 0.9$
5	13.31%	35.64	63.18	97.94	109.09	117.61	126.4	156.43	399.8	459.48
10	11.85%	54.21	104.75	115.92	124.62	132.31	139.52	212.21	419.19	464.87
20	16.19%	112.52	124.36	134.62	142.16	149.63	162.57	362.27	449.08	485.32
30	15.01%	122.92	137.61	148.36	156.12	162.85	170.98	320.82	456.29	488.64

Based on the results of TGA and Table 4, we found that most of the mass loss occurred in the first stage (90–180 °C), and the corresponding conversion rate was mainly at  $x = 0.2$ – $0.6$ . In this stage, the volatilization of organic solvents and lithium salts mainly occurred. The other part of the mass loss occurred in the second stage (400–480 °C), and the corresponding conversion rate was mainly at  $x = 0.8$ – $0.9$ . In this stage, the thermal decomposition of PVDF and separator materials mainly occurred.

In addition, in the first pyrolysis stage (from  $x = 0.2$  to  $x = 0.6$ ), at lower heating rates (5 or 10 K/min), material conversion occurred mainly at lower temperatures generally below 150 °C, while at higher heating rates (20 or 30 K/min), material conversion mainly occurred at higher temperatures mainly above 120 °C. This may be because the heating rate was too fast for the volatilization process to be completely sufficient, which caused the temperature to increase. In the second pyrolysis stage (from  $x = 0.8$  to  $x = 0.9$ ), the temperature range was relatively concentrated around 450 °C.

Finally, according to Table 4 and Equation (4), the linear regression analysis method was used to calculate the reaction activation energy for pyrolysis, as shown in Figure 5. Based on the regression slope, the activation energies for different conversion rates were calculated and are shown in Table 5. Generally, the reaction activation energy of the pyrolysis process was 68.24 kJ/mol on average, which implies that the energy consumption of the pyrolysis industrialization of retired NCM vehicle batteries is not high. In detail, the average activation energy in the first stage of pyrolysis is about 45.43 kJ/mol, and the

average activation energy in the second stage of pyrolysis is about 173.75 kJ/mol, which will provide the data basis for the promotion of industrialization in the future.



**Figure 5.** The linear regression analysis for reaction activation energy calculation.

**Table 5.** The results of reaction activation energy.

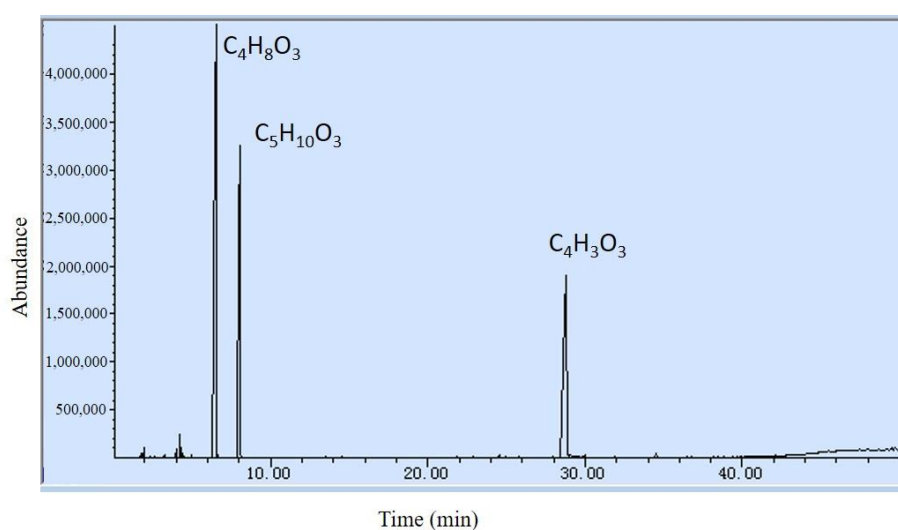
Conversion Rate $x$	Slope $k$	Reaction Activation Energy $E$ (kJ/mol)
0.1	−961.19	17.49
0.2	−1402.81	25.54
0.3	−2431.81	44.27
0.4	−2753.01	50.12
0.5	−2942.72	53.57
0.6	−2944.79	53.61
0.7	−1210.91	22.04
0.8	−6348.81	115.58
0.9	−12,740.46	231.93

### 3.2. Pyrolysis Products and Analysis

#### 3.2.1. The First Stage of Pyrolysis

The internal materials of the vehicle battery extracted from the previous steps (freezing and crushing) were performed in the pyrolysis process and product analysis research. The experiment was implemented in a tube furnace. At the beginning of the pyrolysis experiment, the tube furnace was dried and vacuumed to prevent the combustion of the battery material from reacting with the air during the heating process. Based on the results of TGA, and in order to facilitate the treatment of organic solvents at the low-temperature stage with high efficiency, in this study, a heating rate of 10 k/min was used to reach 150 °C, and the temperature was maintained for 0.5 h.

The gas produced was collected at this stage and the GC/MS method was used to analyze the composition. The results in Figure 6 and Table 6 show that the main composition of the gas consisted of ethylene carbonate (EC), diethyl carbonate (DEC) and ethyl methyl carbonate (EMC), which are common organic solvents for NCM vehicle batteries. The different boiling points of these products can explain why the first stage of pyrolysis covers the conversion  $x$  from 0.2–0.6. Therefore, it can be inferred that in the oxygen-depleted atmosphere, the first-stage (low-temperature) pyrolysis can effectively treat the solvent of waste vehicle batteries. Although these organic solvents are not easy to separate and reuse [25], they are combustible and with high calorific value. Consequently, the gas products in the first stage may be used as fuel for energy recovery in industrial production.



**Figure 6.** The GC/MS chromatogram for pyrolysis product in the first stage.

**Table 6.** The pyrolysis product in the 1st stage.

Composition (Formula)	Peak Area Ratio (%)	Boiling Point (°C)	Calorific Value (kJ/mol)
EC(C <sub>4</sub> H <sub>3</sub> O <sub>3</sub> )	28.94	39	834.0
DEC(C <sub>5</sub> H <sub>10</sub> O <sub>3</sub> )	27.17	126	2708.2
EMC(C <sub>4</sub> H <sub>8</sub> O <sub>3</sub> )	43.14	109	N/A

It should be noted that there is decomposition of the lithium salt at the low-temperature stage, as shown in Equations (1) and (2). Therefore, in the process of industrialization promotion, it is necessary to ensure that the pyrolysis furnace works under negative pressure. At the same time, the furnace and the gas pipeline should be kept dry during the pyrolysis process, and an alkali liquid absorption device may be configured in order to absorb and solidify the fluoride ions, such as the stable form of the CaF<sub>2</sub> precipitate. After the first stage of pyrolysis, the residue of battery internal materials seems to be uneven which have different sizes and shapes as shown in Figure 7a.



(a)



(b)

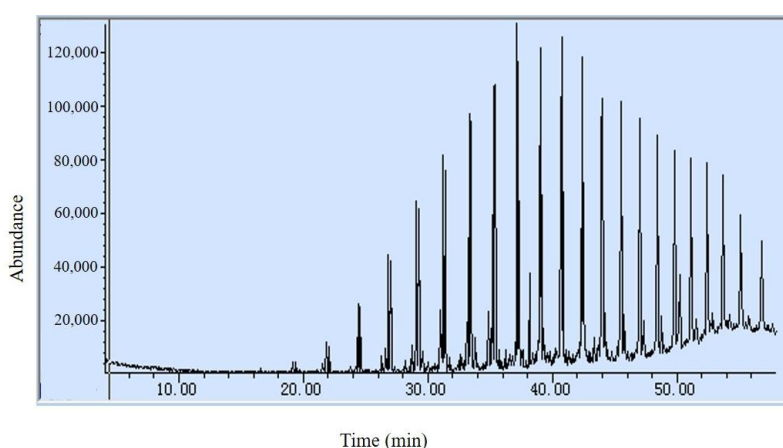
**Figure 7.** (a) The residue after 1st pyrolysis, (b) the residue after 2nd pyrolysis.

### 3.2.2. The Second Stage of Pyrolysis

#### (1) Gas Production Analysis

After the first pyrolysis stage, the internal material was relatively stable. Before the second pyrolysis stage, the material residue was pulverized to facilitate efficiency. The second-stage pyrolysis process was performed in a tube furnace under a nitrogen atmosphere, in which the temperature was raised to 450 °C at 10 k/min, and this temperature was maintained for 0.5 h.

The pyrolysis gas products were collected, and GC/MS was used to analyze the composition. The results in Figure 8 and Table 7 show that the main composition of the gas was N<sub>2</sub> since the pyrolysis process in the second stage is performed in an N<sub>2</sub> atmosphere. Due to the decomposition of separator materials in this stage, many hydrocarbon products with small molecular weight, as well as CO<sub>2</sub> and water, were also generated. In addition, some alkane gas products produced in the second stage also had a considerably high calorific value such as C<sub>2</sub>H<sub>4</sub> (1411 kJ/mol) and C<sub>2</sub>H<sub>6</sub> (1559.9 kJ/mol). Therefore, the gas products in the second pyrolysis can also be considered as a combustible gas for energy recovery.



**Figure 8.** The GC/MS chromatogram for tar in the 2nd stage.

**Table 7.** The pyrolysis gas product in the 2nd stage.

Products	N <sub>2</sub>	CO <sub>2</sub>	H <sub>2</sub> O	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>4</sub> H <sub>8</sub>	C <sub>4</sub> H <sub>10</sub>	C <sub>5</sub> H <sub>10</sub>	C <sub>5</sub> H <sub>12</sub>	C <sub>6</sub> H <sub>12</sub>
Peak area ratio (%)	89.27	3.87	1.73	0.39	0.26	1.11	0.41	0.66	0.50	0.66	0.39	0.91

It should also be noted that due to the decomposition of PVDF in the second temperature stage, fluoride is released. Therefore, in the process of industrialization promotion, it is also necessary to maintain negative pressure to avoid leakage and to ensure good exhaust gas absorption to prevent harm caused by the fluoride. At the same time, because water is generated during the pyrolysis process, it may cause fluoride dissolution, which may corrode the pipe wall. Consequently, it is necessary to strengthen the anticorrosive treatment of the pipeline before the second stage of pyrolysis.

#### (2) Solid Production Analysis

During the second stage of the pyrolysis process, it was found that tar accumulated around the outlet of the tube wall. As a product of thermal cracking, it gradually condensed on the tube wall after leaving the heating zone. Similarly, GC/MS analysis was performed and found that the composition of the product is very complex, mainly including dozens of macromolecular organic hydrocarbons from C<sub>15</sub> to C<sub>36</sub>, and their main peak area ratios are about 1%–3%. Elementary analysis for the tar was performed by EAI analysis, and it was found that the product mainly contained C 85.28%, H 11.48%,

O 1.14%, N 0.56%. Therefore, it can also be inferred that the tar produced by the second stage pyrolysis also has the potential to be used as a fuel.

After two stages of pyrolysis, the internal materials of the NCM vehicle battery seem to be relatively homogeneous, as shown in Figure 7b. Then, ICP analysis was employed to detect the elements' mass percentage in the solid residue. In detail, the nickel (7.91%), cobalt (8.84%), manganese (7.04%) and lithium (3.31%) in the remaining solids mainly come from NCM's cathode material, while copper (17.22%) and aluminum (10.51%) come mainly from copper foil and aluminum foil, which can be recycled or recovered for new battery production.

Generally, this two-stage pyrolysis process completely dealt with the issues of electrolyte, separator and PVDF during battery pretreatment, which obtains the relevant elements of NCM vehicle battery material production. This two-stage process lays a foundation for future subsequent hydrometallurgical or pyrometallurgical processes to recover valuable metals and generate cathode material precursors.

### 3.3. Industrial Process Vision for NCM Vehicle Battery Recycling

An industrial process vision for NCM vehicle battery recycling is shown in Figure 9. After deep-discharge and environmentally friendly automated disassembly and cutting under the  $N_2$  gas atmosphere, the internal material of the battery is extracted. Then, the organic solvent and lithium salt in the electrolyte are processed at a low-temperature stage, and the separator and PVDF are decomposed at a high-temperature stage. The gas products produced at the low-temperature stage and the gas and tar products produced at the high-temperature stage are recovered as fuel. The solid pyrolysis residue includes the metal elements required for battery production.

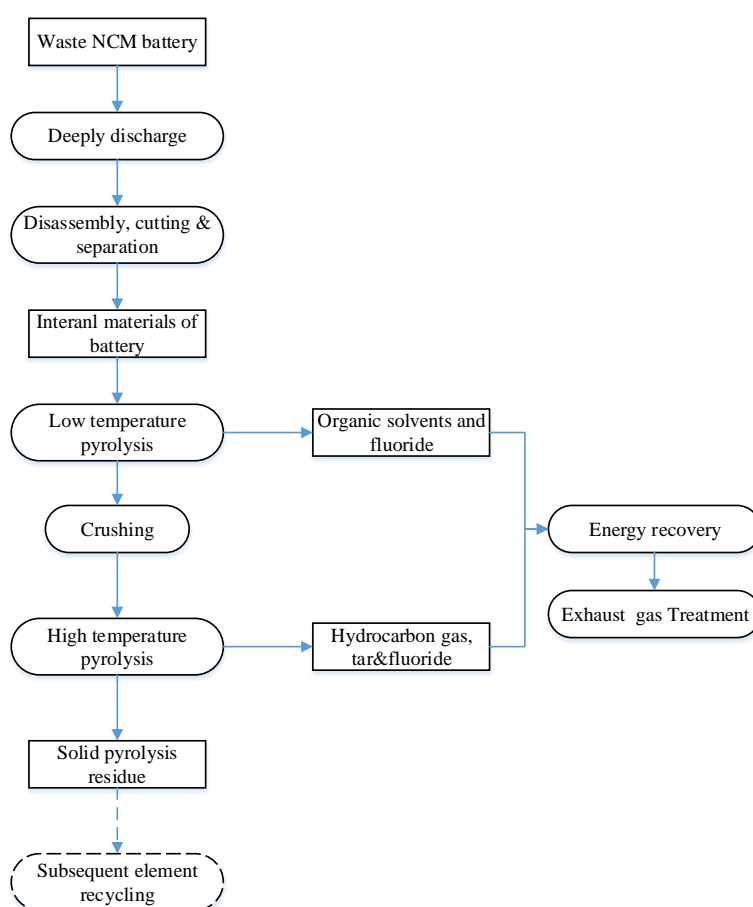
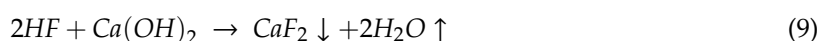
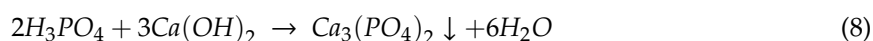
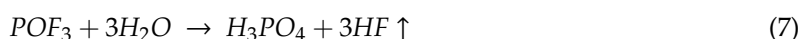
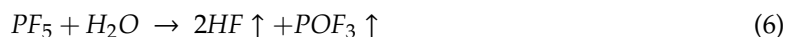


Figure 9. The flow chart of industrial process vision for NCM vehicle battery recycling.

As mentioned in the introduction chapter, the solid residue may be applied by pyrometallurgy or hydrometallurgy methods for valuable metals, such as Co and Ni in the subsequent process. Note that harmful byproducts are generated during the pyrolysis of the battery such as PF<sub>5</sub> and HF from the decomposition of the binder and electrolyte. To deal with them, exhaust gas treatment measures should be configured in the process. For example, it can be considered to absorb and solidify the products of lithium salt decomposition to form a more stable and safe substance, and the reaction process is as follows:



#### 4. Conclusions

In this study, a method was established to improve the pretreatment plans for NCM vehicle batteries, to prevent hazardous electrolytes and to deal with the removal of separator materials. We discussed a two-stage pyrolysis treatment for waste NCM batteries. Through TGA, the pyrolysis temperature in two stages was determined to be 150 °C and 450 °C, respectively. In addition, the feasibility of the pyrolysis process by calculation of reaction activation energy was discussed, and the results give a positive affirmation of 68.24 kJ/mol on average. The pyrolysis products of the two stages were analyzed. It was found that the gas products in the first stage were mainly organic solvents such as EC (C<sub>4</sub>H<sub>3</sub>O<sub>3</sub>), DEC (C<sub>5</sub>H<sub>10</sub>O<sub>3</sub>) and EMC (C<sub>4</sub>H<sub>8</sub>O<sub>3</sub>), which are commonly used for NCM vehicle battery production. In the second stage, the gas products were mainly alkene C<sub>2</sub>–C<sub>6</sub> from the decomposition of separator, and their calorific value is high. At the same stage, the solid products include tar and solid residue. The results show that the tar consists of dozens of hydrocarbons C<sub>15</sub>–C<sub>36</sub> which have a high potentiality as fuel. The ICP detection for solid residue indicates that it consists of nickel (7.91%), cobalt (8.84%), manganese (7.04%), lithium (3.31%), copper (17.22%) and aluminum (10.51%), which can be recycled or recovered for new battery production. It is also worth noting that attention should be paid to the hazards of fluoride to prevent leakage under negative pressure, so it is necessary to keep pipelines dry and to prevent corrosion in the promotion of industrialization in the future. Finally, a flowchart was presented to show the industrial process vision for NCM vehicle battery recycling. Valuable metals such as Co and Ni may be applied by pyrometallurgy or hydrometallurgy methods for recovery, and hazard gas products such as PF<sub>5</sub> and HF can be considered to absorb and solidify by lime water to form a more stable and safe substance.

Therefore, this research can be considered a supplement to the pretreatment and provides a preliminary guarantee for the subsequent metal element recovery process. Furthermore, the method can be extended to deal with LFP waste vehicle batteries with non-aqueous electrolytes and lithium-ion electrolytes and PP/PE-based separator, which occupies the other main part of the vehicle battery market in China.

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