UPCYCLING APPROACH OF POLYVINYCL CHLORIDE WASTE MANAGEMENT

by
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Abstract

In this project, a combination of the non-catalytic dechlorination at 250°C-300°C and the catalytic hydrocracking at ≥ 300°C is proposed as an upcycling approach of polyvinyl chloride (PVC) waste management. According to our experimental results, 100% dechlorination efficiency has been achieved after two runs of the dechlorination process. Our preliminary hydrocracking results indicated 80% of dechlorinated PVC residuals can be converted into hydrocarbons from C2 to C8, with C8 having the highest selectivity of approximately 56%. Heavy-oil-like products were observed after the hydrocracking, and further characterization techniques will be applied to analyze the compositions of the heavy-oil-like products. A preliminary techno-economic assessment of the proposed upcycling approach of PVC waste has been conducted. With electrolysis-generated hydrogen as the feedstock for hydrocracking, the net present value after 20 years of operation will be $26.5 million, and the payback period calculated will be within two years.

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Secondary Reader: Dr. Michael Tsapatsis (Reader)
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1. Introduction

1.1 Background

The advent of plastics in early 20th century has drastically changed our lifestyles and ways of production. Due to various unique properties, different plastic materials have been developed to accommodate specific needs, and thus abundant species of plastic materials are being invented frequently as demands become more complicated and compelling. According to the US Environmental Protection Agency (EPA) report in 2017,1 35.7 million tons of plastics were generated while only 2.96 million tons (8.3%) were recycled along with 5.6 million tons (15.7%) combusted for energy recovery and 26.8 million tons (75.7%) landfilled. Additionally, 26.8 million tons of landfilled plastic waste contributed to 19.2% of municipal solid waste (MSW) landfilled. Based on the report data provided by EPA,2 87% of plastic waste generated can be categorized into five different species: polyethylene (PE, HDPE, LDPE), polyethylene terephthalate (PET), polyvinyl chloride (PVC) and polystyrene (PS). LDPE contributed 23.1% of the MSW plastics produced, following PP with 22.6%, HDPE with 17.4%, PET with 14.2%, PS with 7.1% and PVC with 2.7%. Meanwhile, 31.4% of total MSW plastics recovered were PET along with 20.4% as HDPE, 13.9% as LDPE, 1.4% and 0.7% being PS and PP respectively as shown in Figure 1. Recovery of PVC has been not reported yet. Furthermore, with approximate 30 million tons of MSW plastic generation, the recovery rates of HDPE, LDPE PET, PP and PS are 10.3%, 5.3%, 19.5%, 0.6% and 0.9% accordingly. Among the recovered plastics, bottles, packaging containers, synthetic fibers, toys, electronics, construction and household goods are the common forms. Additionally, even though PP and PS are currently recyclable, their recovery rates are both less than 1%. However, due to rigidity, durability and toxicity of PVC, landfill is currently the most acceptable approach for PVC waste management.
Figure 1. Histograms of MSW plastic category distribution with percentiles of the total production and recovery along with recovery rates associated with different plastic species.

1.2 Established Recycling Routes

There are four established routes for plastic recycling: primary (re-extrusion), secondary (mechanical), tertiary (chemical recycling) and quaternary (energy recovery) recycling approaches. The recycling route types depend on factors such as site locations, physical and chemical properties of plastics and related recycling regulation. Primary recycling refers to the method of re-introduction of homogenous plastic waste into the extrusion cycle without physical and chemical recycling implementation. However, primary recycling is not viable for MSW plastic management due to its complex compositions and contamination. Secondary recycling, as known as mechanical recycling, is only applicable for homogenous and sorted plastic waste. Tertiary recycling involves in chemical recycling leading to formation of raw materials or valuable products, and this method is often referred as upcycling. Quaternary recycling is the energy recovery process which includes incineration and pyrolysis, which is really controversial
due to generation of toxic pollutants such as SO₂, NO₂, volatile organic chlorides (VOC) and dioxins. It is noteworthy that currently all PVC waste is being landfilled. However, in view of our scarce land and earth resources, landfilling PVC is not a sustainable approach, and the landfilled PVC will gradually erode earth and pollute underground water and sea water. Moreover, combustion of PVC as energy recovery is not accepted since VOC, dioxins and hydrochloride (HCl) will be released during the pyrolysis and combustion processes. Tertiary recycling or upcycling is currently the most sustainable approach for PVC waste management.

1.3 Dechlorination Mechanism

Many researchers have shown that the weak thermal stability of PVC is largely attributed to the presence of thermally labile structural segments and defects. Branching and tertiary chlorine are among the important structural defects. Isothermal and linear heating rate methods have been applied to study the kinetic models of PVC thermal dechlorination. In many relevant studies, the established model of PVC thermal degradation involves two processes. The first process refers to the elimination of side groups, which is the dechlorination of PVC. The onset temperature of the first process under inert gas condition is at around 250°C. During the first process, the majority of Cl in PVC is released in the form of HCl, and the PVC will be converted into linear polyene structures. The HCl released during the first process counts for 99% of the total volatile products, and the rest 1% of the volatiles generated are mainly substituted aromatics such as benzene. In the first stage, The generation of unsubstituted aromatics is due to the intramolecular cyclization of linear polyenes. The second process of PVC thermal decomposition occurs at approximately 350°C. During the second stage of PVC thermal decomposition, large amounts of alkyl aromatics are generated, while alkyl aromatics are absent
in the first stage. It is proposed that the intermolecular crosslinking and the intramolecular cyclization of linear polyenes are in concurrence with the production of the substituted aromatics. The intermolecular crosslinking of linear polyenes leads to the formation of crosslinked polyene chains. At high temperature condition ≥350°C, cross-linked polyenes produce alkyl aromatics and chars. The reaction scheme is demonstrated in **Figure 2**.13

**Figure 2.** Reaction scheme of PVC thermal degradation.13

**Figure 3.** The kinetic model of PVC thermal decomposition demonstration.4
The first stage of PVC thermal dechlorination is reported with an activation energy of 114 kJ mol\(^{-1}\), which is described in a nucleation and growth type kinetic model. The second stage follows a diffusion-controlled kinetic model with an activation energy of 202 kJ mol\(^{-1}\).\(^{4}\) The nucleation and growth kinetic model is proposed based upon the presence of the thermally labile sites and structure defects in the PVC at which the reaction initiates and proceeds. The diffusion-controlled mechanism is confirmed by the existence of a sigmoid shape of the heating curve associated with the second stage and supported by the microscopic observation of the bubble formation at the end of the first stage.\(^{4}\) The kinetic models of the PVC thermal dechlorination is demonstrated in the Figure 4. To confirm the literature reports, the thermogravimetric analysis (TGA) of PVC under Ar was conducted (Figure 4). The major mass loss of PVC occurs between around 250\(^{\circ}\)C and 350\(^{\circ}\)C shown below as the pink region of the weight loss percentage curve. The thermal decomposition can be divided into two major stages. The first stage is the dechlorination stage, which also refers to the major mass loss stage as the pink region in Figure 2. The second stage includes the blue, green and yellow regions, which correspond to the decomposition and cracking of the dechlorinated (de-Cl) PVC from 350\(^{\circ}\)C to 600\(^{\circ}\)C. The TGA results are consistent with the proposed kinetic model of PVC thermal degradation.
Furthermore, incineration of PVC will release HCl, VOC and dioxins such as chlorobenzene, polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) shown in Figure 5.\textsuperscript{16} Emissions of HCl and VOC will cause environment issues such as acid rain, building and soil corrosion.\textsuperscript{17} Dioxins are cancer-causing agents and persistent environmental pollutants.\textsuperscript{18} It is important to eliminate the release of HCl, VOC and dioxins. Therefore, inert gas conditions and HCl absorbents are necessary components for clean PVC thermal dechlorination.
1.4 Current Dechlorination Approaches

The two major challenges of clean PVC thermal dechlorination are to realize the effective HCl absorption and to achieve high dechlorination efficiency. In general, there are two effective routes of dechlorination: conventional thermal degradation and hydrothermal treatment. Both methods aim to achieve complete HCl absorption with high dechlorination efficiencies, and recent review article showed that both methods were proven to achieve dechlorination efficiencies of 95% or higher. The dechlorination efficiency is expressed as

\[
\text{Dechlorination Efficiency} = \frac{\text{Mass of Cl in HCl}}{\text{Mass of Cl in PVC}} \times 100\% \quad (1)
\]

The thermal PVC dechlorination in fixed-bed reactor setups has been widely investigated over the years. One major problem associated with the thermal PVC dechlorination is the generation of Cl-containing products, and the Cl content in the products makes it difficult to realize upcycling of PVC wastes. Many researchers proposed the catalytic dechlorination, which involves the selective cleavage of C-Cl bonds. The catalytic dechlorination can lower the toxicity of the products and generate valuable and reusable raw materials.
often requires the participation of metal oxides and silica-alumina zeolites such as CaO and ZSM-5 serving as both catalysts and HCl absorbers. The catalytic dechlorination involves two processes. The first process (the two-stage process) is the thermal dechlorination as described in the dechlorination mechanism section. The second process is the conversion of dechlorinated PVC into Cl-free hydrocarbon products.\textsuperscript{19} Sakata et al (2003)\textsuperscript{19} reported that during the two processes of the catalytic dechlorination, oil yield in the first stage of pyrolysis contained 0.2wt% chlorine, while in the second stage, various iron-based catalyst exhibited high dechlorination performance. Additionally, in their report, a Ca-C catalyst was in the single-step degradation and catalytic process, and the oil product contain 360ppm chlorine content, yet the amount of chlorine was reduced to zero when using a Ca-C sorbent. In a similar study,\textsuperscript{20} PVC pyrolysis was categorized into four different approaches: (1) conventional thermal pyrolysis; (2) conventional catalytic pyrolysis; (3) catalytic stepwise pyrolysis; (4) non-catalytic dechlorination and catalytic pyrolysis. ZSM-5 catalyst was used as the cracking catalyst in their study. According to their results, the gas yield of the combination of the non-catalytic dechlorination and catalytic pyrolysis was highest. Conventional catalytic pyrolysis produced similar amount of the gas yield with the combination of the non-catalytic dechlorination and catalytic pyrolysis. The gas yield of the catalytic stepwise pyrolysis alone was lower than the former two processes. The conventional thermal pyrolysis generated the least gas yield. The gas yield sequence was due to the fact that zeolite catalysts lost some catalytic activity during the dechlorination because of the PVC melting. The melting of PVC could physically block the catalytic pores. In their report, the yield of heavy carbons increased up to 9.5wt% for the catalytic stepwise pyrolysis, which confirmed the activity loss of the zeolite catalysts. For the combination of the non-catalytic dechlorination and catalytic pyrolysis, the Cl content in the liquid hydrocarbon products was the lowest.
Therefore, an optimal process of PVC waste upcycling would be the combination of an initial low-temperature (250°C-350°C) dechlorination without catalyst yet with HCl absorbent, and a following catalytic pyrolysis at high temperatures (≥350°C). \(^3,20\)

The critical water (CW)/ subcritical water (SCW) system has been attracting researchers’ interests recently in heavy oil upgrading and desulfurization.\(^{21,22}\) The CW/SCW hydrothermal treatment has advantages of fast reaction rates and homogenous reactions without the mass transfer limitations. The short-chain hydrocarbons during pyrolysis can be dispersed in solvent, and thereby reduce the formation of coke.\(^{23}\) Many studies have been conducted on hydrothermal treatment of PVC with CW/SCW.\(^3\) The hydrothermal treatment takes place in pressurized autoclave reactors while in lower temperature ranges from 200°C to 300°C at pressures ≥3MPa. Xiu et al (2014)\(^{24}\) reported that at below 200°C, no noticeable dechlorination was observed, while the dechlorination efficiency increased to 93% at 250°C, which eventually reached close to 100% at 300°C. A similar study was conducted by Kubátová et al. (2002).\(^{25}\) In their study, mass loss of PVC only occurred at above 250°C. Approximately 44wt% of PVC was calculated as mass loss at 300°C and 370°C, which is in agreement with the results from Xiu et al (2014). Additionally, the remaining 56wt% of PVC lost further confirmed the complete dechlorination. In addition, GC/MS was reported to detect no chlorinated hydrocarbons in the liquid product, and it was proposed that conjugated alkenes were present in the residuals after the hydrothermal treatment. Furthermore, the formation of conjugated alkenes was consistent with the dechloriantion mechanism of the thermal dechlorination.

Both thermal dechlorination and hydrothermal treatment demonstrated the viability of PVC waste upcycling. In view of our current laboratory apparatus and capacity, the combination of an initial low-temperature (250°C-350°C) non-catalytic dechlorination with HCl absorbent,
and a following catalytic pyrolysis at high temperatures (≥350°C) was selected as our upcycling approach of PVC waste management. The overview of the proposed upcycling approach of PVC waste management is demonstrated in the Figure 6.

Figure 6. The overview of the proposed upcycling approach of PVC waste management.
2. Experimental Section

2.1 Experimental Setup

The scheme of the overall experimental setup is demonstrated below (Figure 7):

Figure 7. PVC waste upcycling experimental setup.
Both dechlorination and hydrocracking processes were conducted in the same tubular furnace reactor manufactured by ThermoCraft. The tubular furnace reactor consists of a heating jacket with thermocouples embedded and a quartz tube reactor customed to cater to the specifications of the furnace design (Figure 8). The electric power of the furnace is 200W.

The gas chromatography (GC-2010 Plus, Shimadzu) equipped with a barrier ionization discharge (BID) detector and the SH-Rt-Q-Bond column was employed for GC analysis of the products (Figure 9).
Figure 9. Gas Chromatography (GC-2010 Plus, Shimadzu) equipped with a barrier ionization discharge (BID) detector and the SH-Rt-Q-Bond column.

The CI-NMR characterizations of the prepared CI-NMR samples were performed on Bruker UltraShield 400MHz/54mm bore (Figure 10).

The thermogravimetric analysis (TGA) was conducted on Mettler Toledo Thermogravimetric Analyzer. ThermoNicolet Nexus 670 FTIR Spectrometer was utilized to conduct the Fourier-transform infrared spectroscopy (FTIR) shown in Figure 11.
Figure 10. Bruker UltraShield 400MHz/54mm bore.
The pure polyvinyl chloride particles with average molecular weight of ~62,000 (CAS number: 9002-86-2) and 98%-purity calcium oxide with ≤ 160nm particle size (BET) (CAS number: 1305-78-8) were purchased from Sigma Aldrich. 99.9% deuterium oxide (CAS number: 7789-20-0) purchased from Sigma Aldrich was as the deuterated solvent for Cl-NMR sample preparation. 40-60 mesh sieve was manufactured by Cole-Palmer.
2.2 Experimental Modification

Figure 12. The original mixture configuration (left) and the layered configuration (right).

In our original reactor tube setup, a mixture of CaO, PVC and quartz sand were added into the reactor. In the first stage of thermal degradation, melted PVC was stick to the surface of CaO and quartz sand, which leaded to particle aggregation and caused blockage of the gas pathway (Figure 12 and Figure 13). The blockage of the gas pathway induced pressure build-ups on the upper half of the reactor tube and might cause gas backflow into the gas storage tank, which would become serious safety hazards. Furthermore, it is difficult to separate de-PVC and CaCl₂/CaO from the residuals. It is known that in a heterogeneous reaction, mass transfer of the reactants start from the bulk fluid to the surface the pellets. The effective diffusivity includes three factors. First, not all of the area normal to the direction of the flux, especially the area
occupied by solids, is viable for molecules to diffuse. Second, the paths are tortuous. Third, the pores have varying cross-sectional areas. To achieve the effective diffusivity, sieving of all solid particles involved in the PVC thermal degradation into 40-60 mesh will be applied. The sieved particles will maintain within the proper range of diameters for the effective diffusivity. In addition to sieving, a layered configuration was used to replace the original configuration since calcium-based absorbents exhibited catalytic activities during thermal PVC dechlorination, which inhibited the formation of HCl and promoted the generation of chlorinated aromatics. Therefore, a layered reactor tube configuration of sieved particles was adopted into the experimental setup to replace the original reactor tube configuration.

Figure 13. The image of the mixture configuration before the thermal dichlorination.
Figure 14. The image of the layered configuration after the thermal dechlorination before hydrocracking.
2.3. PVC Upcycling Experiment

For the dechlorination process, 250mg of 40-60 mesh PVC particles was sandwiched by two small pieces of quartz cotton on the top half of the quartz reactor tube, and 300mg of 40-60 mesh CaO were filled in the reactor tube from the bottom end and closed by another small piece of quartz cotton. The experimental setup is demonstrated in Figure 14.

Before the dechlorination process, 30ccm of pure N2 flowed through the reactor for 10 minutes to expel the remaining air in the quartz tube and maintain an inert-gas-only atmosphere. Gas leakage test was conducted to confirm the adequate gas tightness in the system. Alicat gas flow controller was used to adjust the flow rates of the gas. After 10 minutes of N2 flow, the temperature program connected to the furnace was set to 250ºC with a ramp rate of 5ºC/min, and the dwell time was set to 30 minutes.

After the first dechlorination, the CaO/CaCl2 residuals were extracted from the bottom half of the quartz tube, and 25mL of deionized water was used to dissolve the residuals. The mixture was transferred in a 50mL centrifuge tube and centrifuged for 5 minutes at 10,000rpm. The separated clear solution after centrifugation was obtained via filtration. The clear solution was saved for further characterizations. A second dechlorination was conducted with the same procedures to assure the complete dechlorination. After each dechlorination run, Cl-NMR and FTIR were conducted to check the chlorine content absorbed by CaO and the intensity of C-Cl stretching in the de-Cl PVC residuals respectively.

After the second dechlorination, 50mg of 40-60 mesh H-ZSM5 was added into the bottom half of the quartz tube and closed with a small piece. Prior to the onset of the hydrocracking process, 30sccm of pure N2 flow was required to flow through the reactor tube for at least 10 minutes to get rid of the air content. Gas tightness was conducted thoroughly for the
entire system. Once the gas tightness was confirmed, 30 sccm of 5% H₂/N₂ was switched to flow through the quartz tube for 10 minutes. After 10 minutes of 5% H₂/N₂ flow, the temperature program was set to 350°C with a ramp rate of 5°C/min for 60 minutes. The outlet stream was connected to a gas chromatography (GC) analyzer to analyze the product compositions and distributions.
3 Experimental Results

3.1 PVC Dechlorination Results

In our experimental setup, we conducted a non-catalytic dechlorination, and HCl will be the main product during the dechlorination process. Thereby, the degree of dechlorination could be quantitatively analyzed by the amount of HCl absorbed by CaO. After HCl absorption, CaO became CaCl₂. Commonly, quantitative analysis of chloride content in aqueous solution was conducted via silver nitrate (AgNO₃) titration. However, since silver nitrate is very light sensitive, continuous running silver nitrate titration on a daily basis to quantify chloride was not ideal for us in both technical and economic standpoints.

To achieve consistent and reliable chloride ion quantification, Chlorine-nuclear magnetic resonance (Cl-NMR) was utilized. Cl-NMR can detect the presence of chloride ions in deuterated solvents such deuterated water and deuterated ethanol. A normal Cl-NMR sample will use NaCl as the internal standard, yet the addition of NaCl into our Cl-NMR will interfere with our results. Therefore, we decided to first establish a standard calibration curve with different concentration gradient of NaCl aqueous solutions with deuterated water (D₂O). Standard NaCl solution with concentrations of 1000ppm to 5000ppm were prepared. 700uL of each solution was extracted into five 5mm OD Wilmad 521-ASST-100 quartz tubes, and 100uL of D₂O was added into each sample tube. Cl-NMR characterizations of all five samples were conducted on Bruker UltraShield 400MHz/54mm bore. The standard calibration curved was obtained based on the correlation of the signal intensity and the concentration. The standard calibration curved was shown in Figure 15.
After the standard calibration curve was established, 25mL of de-ionized water was used to dissolve the after-reaction CaO/CaCl$_2$ residues, and the mixture was transferred into a 30mL centrifuge tube. The sample was centrifuged at 10,000rpm for 5 minutes. After centrifugation, 700uL of the upper clear solution was extracted into a 5mm OD Wilmad 521-ASST-100 quartz tube. 100uL of D$_2$O was added into the sample tube. The Cl-NMR characterizations of the prepared Cl-NMR samples were conducted, and one of the Cl-NMR spectra were shown in Figure 16. As shown in Figure 16, after the second dechloriantion run, there was no Cl ion signal detected, which was different from the patterns of the first dichlorination. Additionally, we added CaO in the bottom half of the reactor during the hydrocracking after the second dechlorination run, and the absence of the Cl ion signal indicated that there was no HCl formed.
after the second dechlorination. In other words, the dechlorination of PVC by releasing HCl was completed after two runs.

Figure 16. Cl-NMR of CaCl$_2$ solution after 1$^{st}$ dechlorination, 2$^{nd}$ dechlorination, and hydrocracking at 350ºC.

Based on the dechlorination efficiency equation mentioned in Section 1.4, we proposed an adapted version of dechlorination efficiency based on our experimental parameters, which was the percentage of Cl in PVC absorbed by CaO. The highest single-run dechlorination efficiency with only CaO as the absorbent was calculated to be 92.1%, and after a second dechlorination run, a 100% dechlorination efficiency was achieved (Table 1). Additionally, although CaO exhibited higher Cl absorption than CaCO$_3$, CaCO$_3$ would be a better HCl
absorbent from an economic perspective if the upcycling approach could be scaled up. Since our
dechlorination approach was non-catalytic, the absorbents placed in the bottom half of the
reactor tube would not affect the actual dechlorination efficiency.

**Table 1.** Dechlorination efficiencies with different absorbents.

<table>
<thead>
<tr>
<th>Experiments</th>
<th>Cl Absorbed (mg)</th>
<th>Dechlorination Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC + CaO</td>
<td>128.9</td>
<td>92.1</td>
</tr>
<tr>
<td>PVC + CaCO₃</td>
<td>126.5</td>
<td>89.2</td>
</tr>
<tr>
<td>PVC + CaO + H-ZSM5</td>
<td>131.0</td>
<td>93.6</td>
</tr>
</tbody>
</table>

To confirm our dechlorination results, PVC, deCl-PVC, HDPE and LDPE samples were
sent for FTIR characterization. FTIR was often used a characterization method to obtain an
infrared spectra of absorption of a gas, liquid and solid, and many researchers used FTIR as a
major characterization method to check the existence of certain functional groups in polymer.²⁷
As shown in **Figure 17**, aliphatic groups of CH (2900 – 3000cm⁻¹), CH₂ (1450 – 1500cm⁻¹) CH₃
(1350 – 1400cm⁻¹) were spotted. The peaks between 2800 m⁻¹ and 3000 m⁻¹ referred to the
existence of -CH₁, -CH₂, -CH₃ functional groups, and the patterns between 500cm⁻¹ and 700cm⁻¹
were associated with C-Cl stretching vibrations. The appearance of the deCl-PVC residuals was
black and granular as shown in **Figure 18**.
Figure 17. FTIR diagram of PVC, deCl-PVC, LDPE and HDPE with ATR settings.
Figure 17. The FTIR pattern of PVC exhibited the characteristic C-Cl stretching between 500cm\(^{-1}\) and 700cm\(^{-1}\), and the CH\(_2\) (1450 – 1500cm\(^{-1}\)) pattern was spotted, which was in agreement with the existing functional groups in PVC monomer. The FTIR pattern of deCl-PVC, on the other hand, did not exhibit the characteristic C-Cl stretching in the range of 500cm\(^{-1}\) and 700cm\(^{-1}\), and the peaks between 2750cm\(^{-1}\) and 3000cm\(^{-1}\) referred to the -CH\(_3\), -CH\(_2\), and -CH
functional groups. Furthermore, the peak patterns of deCl-PVC residuals were also different from those of LDPE and HDPE. In other words, the deCl-PVC residuals contained different function groups from LDPE and HDPE, and the deCl-PVC residuals were most likely linear alkenes. The absence of the characteristic C-Cl stretching in deCl-PVC residuals confirmed the complete dechlorination, which was in agreement with the Cl-NMR results.

According to Cl-NMR and FTIR results, Cl in PVC was completely removed after the second dechlorination run, and the deCl-PVC residuals exhibited the similar patterns as alkenes, which was in agreement with the dechlorination mechanism described in Section 1.3.

3.2 deCl-PVC Hydrocracking Results

The hydrocracking products were analyzed via Shimadzu GC-2010 Plus equipped with an SH-Rt-Q-BOND column and a BID detector. Based the GC results, the hydrocracking conversion of deCl-PVC residuals was 80% and product selectivity was demonstrated in Figure 19. The product selectivity of C8 was 65%, and that of C7 was 18%. Due to COVID-19 situation, we could not repeat the experiments and conform the product selectivity with sufficient trials.
The remaining 20% of deCl-PVC products were speculated to be fixed carbon and hydrocarbons of C12 and heavier according to the observation of the after-hydrocracking quartz tube shown in Figure 20. The light-brown to dark-brown heavy-oil-like products could be rinsed off with benzene and toluene, which meant that the heavy-oil-like product contained hydrophobic functional groups, especially aromatic functional groups. Further H-NMR could be used as a useful characterization to perform a preliminary qualitative analysis of the heavy-oil-like products.

Figure 19. The product selectivity of deCl-PVC hydrocracking with 80% conversion.
Figure 20. The image of the heavy-oil-like products left on the reactor tube after the hydrocracking of deCl-PVC.

The circled brown oil-like products could be hydrocarbons of C12 or heavier. However, due to the limitation of our current GC column and the abrupt COVID-19 pandemic situation, the
products cannot be further analyzed. However, we plan to conduct high-temperature gel-permeation chromatography (GPC) to check the molecular weight of the oil product, analyze product distribution and selectivity on GC with a new column (Rtx-1, 30m, 0.53mm ID 0.25μm) designated for C10+ product detection, and solid-state NMR (ssNMR) to analyze the functional groups in the oil product.
4. Discussion

4.1 Studies of the PVC Dechlorination Dependence on Temperature

According to the TGA conducted by López et al., the effect of time and temperature on PVC dechlorination under inert gas conditions was demonstrated in Table 2.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Time (min)</th>
<th>Total Weight Loss (wt%)</th>
<th>Cl loss (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>90</td>
<td>41.1</td>
<td>94.0</td>
</tr>
<tr>
<td>250</td>
<td>120</td>
<td>43.7</td>
<td>94.8</td>
</tr>
<tr>
<td>275</td>
<td>60</td>
<td>50.4</td>
<td>96.9</td>
</tr>
<tr>
<td>300</td>
<td>30</td>
<td>54.1</td>
<td>99.2</td>
</tr>
</tbody>
</table>

According to our TGA report (Figure 4), the dechlorination did not take place until temperature reached at 250°C. Based on the results shown in Table 2, there was no significant weight loss change of chlorine content at 250°C as the reaction time prolonged from 90 minutes to 120 minutes. In other words, the reaction time did not affect the dechlorination efficiency as much once the onset temperature was reached. At 300°C, the highest chlorine weight loss of 99.2% was achieved at 300°C with a reaction duration of 30 minutes. In addition, our experimental results showed that two or more runs at relatively low temperature conditions around 250°C under inert gas could realize the complete dechlorination as shown in the previous FTIR spectra. In other words, a second dechlorination run at 300°C within 30 minutes could achieve 100% dechlorination efficiency. Therefore, 300°C is the ideal temperature to achieve the
highest dechlorination efficiency, and the complete dechloriantion can be finished for the shortest reaction period.

### 4.2 Effects of Calcium-based Additives during PVC Dechlorination

Calcium-based absorbents such as CaO and CaCO₃ have showed the catalytic effect of fixing Cl in forms of chlorinated aromatics like chlorobenzene when mixed with PVC during pyrolysis. In other words, the addition of calcium-based alkaline absorbents will reduce the generation of HCl gas, and simultaneously decrease the fixation of Cl as CaCl₂. Formation of chlorinated aromatics will reduce the dechlorination efficiency calculated based on our established model.

However, chlorobenzene is a common raw material in industrial applications, and fixation of Cl in PVC in forms of chlorobenzene or other chlorinated aromatics with high market values could be another viable of PVC waste upcycling since the amount of PVC waste is relatively low in comparison with other plastic waste species. Our future research focus will be put on the conversion of PVC into valuable chlorinated aromatics during thermal degradation and the marketability of the alternative upcycling approach.

### 4.3 Studies on deCl-PVC Hydrocracking

Based on our preliminary results, deCl-PVC hydrocracking with H-ZSM5 catalyst yielded various species of hydrocarbons. During hydrocracking, zeolite catalyst like H-ZSM5 exhibited the catalytic activity of cracking linear alkenes into short-chain hydrocarbons. The key parameters associated with the zeolite catalyst are the total number of acid sites and the number of accessible acid sites. The mechanism of polyolefin hydrocracking with H-ZSM was derived from the Haag-Dessau’s 1984 mechanism of protolytic alkane cracking. In the Haag-Dessau
mechanism, at high temperature conditions, “a zeolite catalysts protonate an alkane to give carbonium ion transition states that collapse to give alkanes (or dihydrogen) and carbenium ions which give back protons to the catalyst to form alkenes.”29 The common hydrocracking products with H-ZSM5 catalysts are C1-C4 products. However, from our deCl-PVC hydrocracking results, C8 was found to be the most abundant followed by C7 being the second most abundant, and C2-C4 products only had product selectivity of 10%. The phenomenon could to be attributed to the formation of chlorinated aromatics and xylenes as explained in the PVC thermal decomposition mechanism in (Figure 2). Due to COVID-19 situation, few sets of data from PVC hydrocracking was available, and it was hard to confirmed the product selectivity and the overall conversion.

Furthermore, many researchers have been paying much attention on recovering plastic wastes into potential fuel sources.3, 30, 31 Upcycling or recovery of polyethylene into value-added products have been widely studied. Pt-doped perovskite catalysts, mesoporous SBA-15 and ZSM-5 catalysts all exhibited the catalytic activity of converting polyolefins into gasoline-type products via hydrocracking. As increasing focus is being upon this topic, product selectivity becomes an important evaluation of a proposed upcycling approach. Studies have shown that catalytic pyrolysis with porous catalysts could generate a large proportion of aromatic compounds such as benzene and xylene and liquid hydrocarbons.30 Generation of C8+ products seemingly became the hottest topic of upcycling of polyethylene. Similarly, as our hydrocracking results indicated that hydrocracking of deCl-PVC demonstrated the potential of producing xylene-like C8 products and other heavy oil products. Since the product selectivity is being recognized as the indication of the technical feasibility of an upcycling approach, porous catalysts such as SBA-15, SDUSY, ZSM5 catalysts are becoming increasing attractive.30 In our
future hydrocracking experiments, we will vertically compare the catalytic activity of different porous catalysts and evaluate the product selectivity of each catalyst. Building a thorough understanding of catalytic polyolefin hydrocracking will help us re-examine the feasibility of our proposed upcycling approach. Continuation of investigation on deCl-PVC hydrocracking could provide us more insights of alternative approaches of upcycling.

4.4 Techno-Economic Assessment of the Proposed PVC Upcycling Approach

The Techno-Economic Assessment (TEA) of the proposed PVC upcycling approach was conducted based on our experimental results, ASPEN simulations and the state-of-the-art TEA model of plastic waste pyrolysis for production of heavy fuel substitute.32

Table 3. represents the breakdown of the general TEA parameters. The feedstock of PVC waste in our TEA model was chosen to be 10,000 tons per year, and the plant year was designated to be 20 years. The total capital cost, the total operation cost and the utilities cost were estimated based on the corresponding costs of a yield-shift reactor, a heat exchanger network and a separation tower generated by ASPEN Process Economic Analyzer. Two different hydrogen feedstock sources were taken into account: steam-methane-reforming (SMR) generated hydrogen gas and electrolysis generated hydrogen gas. Two sets of raw materials costs were calculated for the two different hydrogen supplies. The product sales were calculated based on the current average market values for light hydrocarbons (C2-C4) and heavy hydrocarbons (C5-C10).
### General Techno-Economic Assessment Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plant life</td>
<td>20 years</td>
</tr>
<tr>
<td>Plant annual operating hours</td>
<td>8760 hours/year</td>
</tr>
<tr>
<td>Total Capital Cost (10,000 tons PVC Waste/year Capacity)</td>
<td>$3,216,570</td>
</tr>
<tr>
<td>Total Operating Cost</td>
<td>$2,826,500/year</td>
</tr>
<tr>
<td>Total Raw Materials Cost (SMR-H₂-Feed)</td>
<td>$452,958/year</td>
</tr>
<tr>
<td>Total Raw Materials Cost (Electrolysis-H₂-Feed)</td>
<td>$1,230,636/year</td>
</tr>
<tr>
<td>Total Product Sales</td>
<td>$7,592,960/year</td>
</tr>
<tr>
<td>Total Utilities Cost</td>
<td>$39,892/year</td>
</tr>
</tbody>
</table>

#### Total Raw Materials Cost Breakdown

<table>
<thead>
<tr>
<th>Feed Cost Description</th>
<th>Cost (year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SMR-H₂ Feed Cost</td>
<td>$263,010/year</td>
</tr>
<tr>
<td>Electrolysis-H₂ Feed Cost</td>
<td>$1,040,688/year</td>
</tr>
<tr>
<td>PVC Waste Feed Cost</td>
<td>$150,000/year</td>
</tr>
<tr>
<td>N₂ Feed Cost</td>
<td>$20,780/year</td>
</tr>
<tr>
<td>Zeolite (H-ZSM5) Feed Cost</td>
<td>$19,168/year</td>
</tr>
</tbody>
</table>

#### Total Product Sales Breakdown

<table>
<thead>
<tr>
<th>Product Sales Description</th>
<th>Cost (year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂-C₄ Product Sales</td>
<td>$552,960/year</td>
</tr>
<tr>
<td>C₅-C₁₀ Product Sales</td>
<td>$7,040,000/year</td>
</tr>
</tbody>
</table>

In our TEA, the taxation and other overhead fees were not considered. A discount rate of 10% was considered for the net present value calculations. The net present values (NPVs) for two hydrogen-feed models are demonstrated in Figure 21 and Figure 22, and the payback periods of both models were within two years. After 20 years of operation, SMR-H₂ feed model is expected have an NPV of $33.2 million, and electrolysis-H₂ feed model will have an NPV of
$26.5 million. Despite the lower costs of SMR-generated H\textsubscript{2} and higher NPVs, utilization of the SMR-generated H\textsubscript{2} will induce more carbon footprints in its manufacturing process. Nevertheless, the electrolysis-generated H\textsubscript{2} sources exhibited environmentally benign properties and promotes the sustainability for environment because of zero CO\textsubscript{2} emission during water electrolysis. Overall, based on our preliminary TEA, the proposed PVC waste upcycling approach demonstrates great market potential and high profitability.

Figure 21. Net present values over 20 years for the SMR-H\textsubscript{2} feed model.
It is noteworthy that our upcycling approach was a combination of the non-catalytic thermal dechlorination and the catalytic hydrocracking. We might neglect the market potential of producing chlorinated aromatics such as chlorobenzene. Chlorobenzene is a valuable chemical raw material, and since the current generation of PVC waste was relatively in comparison with other plastic waste species, upcycling of PVC into chlorobenzene could still be a sustainable approach. Moreover, generation of chlorobenzene does not necessarily require a hydrocracking process as described in the PVC thermal degradation mechanism. Thus, we need to conduct experimental trials on the catalytic thermal degradation of PVC without introduction of a hydrocracking process.

**Figure 22.** Net present values over 20 years for the electrolysis-H₂ feed model.
5. Conclusions and Future

Different chemical recycling approaches of PVC waste management were summarized in this thesis. Both conventional thermal degradation of PVC and hydrothermal treatment have been widely studied by many researchers, and the advantages and disadvantages were discussed in this thesis.

In general, the thermal degradation of PVC involves two stages. The first stage is the dechlorination stage occurring at temperatures 250°C-300°C. During the first stage, Cl content will be released from PVC in the form of HCl. At the completion of the first stage, linear alkene residuals were formed. The second stage involves the intermolecular crosslinking and the intramolecular cyclization of linear alkenes, which are in concurrence with the production of the substituted aromatics. The second stage takes place at ≥ 300°C. At the end of the second stage, light hydrocarbons, alkyl aromatics and char are formed.

The proposed upcycling is the combination of the non-catalytic thermal dechlorination and the catalytic hydrocracking of deCl-PVC residuals. According to our experimental results, near complete dechlorination was achieved after two runs of dechlorination at 250°C, and the results were confirmed by absence of C-Cl stretching in FTIR spectra and the absence of Cl ion signal in Cl-NMR. In order to achieve complete dechlorination within shorter reaction periods, 300°C will be set as the optimal dechlorination temperature for future studies. Based on the catalytic hydrocracking results, 80% of deCl-PVC residuals were converted into C2-C8 hydrocarbons. Among the detected hydrocracking products, C8 had the highest product selectivity of 56%, and C8 formed was speculated to be xylene. 20% of the undetected hydrocracking products can be attributed to char and heavy oil products left on the reactor tube.
Due to COVID-19 situation, no further investigations and characterizations of the products could be conducted.

The proposed upcycling approach in this project demonstrates a viable sustainable recycling route of PVC waste and a market potential according to our experimental results and preliminary TEA. Further optimizations of the upcycling approach setups will be conducted as well as a comprehensive TEA.

![Diagram](image-url)

**Figure 23.** The overview of the proposed upcycling approach for mixture of plastic waste.

Our future efforts will be put into incorporate mixture of plastic waste including HDPE, LDPE, PET, PP, PVC, PS and other MSW plastics into our upcycling approach setup (Figure 23). Eventually, our goals are to eliminate the release of toxic materials, to convert the waste into valuable resources, and to achieve sustainability.
Reference:


Curriculum Vitae

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