

# Systematic Study to Convert Polyvinyl Chloride Waste into Commercial Chemicals

Abduel Majid K. Najjar, Mohamed A. Elmelah, Rashid S. R. Ltayef, and Fahima N. Abudher

**Abstract**—Polyvinyl chloride (PVC) waste is considered one of the environmentally hazardous plastic materials accumulating in huge quantities in landfills. This work was conducted for the purpose of using green chemistry techniques to convert the PVC waste into other chemicals that could be used for commercial purposes. Pyrolysis process of the PVC waste was carried out under inert atmospheric condition. The effect of grain size, temperature and heating time on the amount of evolved hydrogen chloride gas (HCl) was investigated. More than 95% of theoretical calculated amount of HCl was evolved before any emission of any other organic fumes. The evolved HCl was trapped and converted into concentrated hydrochloric acid (11.22 M) and then to a highly pure sodium chloride salt. The residual black material was heated further to remove and trap oily organic fumes. About 14% of initial PVC weight was found to be as heavy metals free oil and may be used as fuel. Finally, 27.74% of the degraded PVC remained as carbon black. The carbon black was grounded and acid digested to remove and determine heavy metal ions content.

**Index Terms**—PVC waste, pyrolysis process, thermal degradation, organic fumes, black carbon.

## I. INTRODUCTION

Waste in general, is an inevitable byproduct of all human development and culture activities, and is directly proportional to the consumption of resources. Population and economic growth not only lead to increase in volume of waste but also to great changes in its specification and contents. There is tremendous increase in some nonbiodegradable contents, particularly plastic waste, which contain polyvinyl chloride (PVC). PVC waste has attracted great attention because cannot be decomposed in nature and hence its safe disposal is creating extraordinary technical, health, environmental, economic, political and social problems [1]. PVC is one of the most widely accumulated plastic materials in landfills after end-life uses and became an active area of scientific research for the objective of creating a proper Solid Waste Management System. The methods and the technologies of recycling of PVC waste have been reviewed [2], [3]. It seems that the recycling of PVC waste into new items and reducing the waste accumulation is still

very limited. Thermal degradation of PVC waste and its conversion into other commercial chemicals could be the best technical solution.

Many works have been reported on the pyrolysis process and kinetics of PVC waste pyrolysis at different temperatures and heating rates [4]-[8]. Saeed and his coworkers studied slow pyrolysis of PVC in fluidized bed reactor at different temperatures [9]. They found that the release of most of chlorine and other organic compounds was dependent on heating temperature. In the PVC matrix, the C-Cl bonds in the structure have a relatively lower binding energy than both the C-C and C-H bonds [10], [11]. This fact proves that the bonds of chlorine with carbon atom in the PVC chains are broken first lead to dichlorination in the first stages of the thermal degradation. Generally, PVC material is characterized by having a very poor thermal conductivity. In the first stages of thermal degradation of large PVC particles, the release of chlorine followed by thermal crosslinking of the outer surface layer may forbid the further dechlorination at the same temperature and the formation of organic vapors. The thermal degradation of small sized PVC particles may lead to fast release of HCl gas at a particular temperature. In order to maintain fast release of HCl gas and eliminate the emission of the organic compounds resulted from the thermal degradation of PVC waste, optimized the experimental conditions are extremely needed. This work aims to study the effects of PVC waste particle size, heating temperature and heating time on the quantitative liberation of pure HCl before any emission of organics, prepare HCl solution and harvesting residual carbon black under controlled experimental conditions. It is known that PVC degrades at relative high temperature producing hydrogen chloride and polyene chains, followed by thermal crosslinking and then initiation of the polymer chain scissions. To avoid any reaction with oxygen, the dehydrochlorination process was carried out under nitrogen atmospheric condition.

## II. MATERIALS AND METHODS

### A. Materials

Samples used in this work were PVC waste collected from National Company for manufacturing of Plastic pipes located in Janzur west of Tripoli-Libya. The PVC waste were washed with tap and distilled water to remove any sand and dirt, oven dried at 60 °C, grounded to 0.5 – 4.0 mm particle sizes using FBM 8000W DIS20402068 grinder and then sieved to specific particle size.

### B. Thermal Decomposition of PVC Waste

A closed glass setup consisted of three necked round

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bottomed flask fitted with a condenser connected to three parallel trap flasks, thermometer, inert gas supplied (nitrogen of 99.60% purity) at 100 ml/min flow rate and thermostatic heating mantle is assembled. Two trap flasks filled with toluene for organic vapors and NaOH solution or H<sub>2</sub>O for HCl gas. The setup was preheated to 200 °C prior to introduction of PVC waste sample (5.0 g) into the flask and the heating continued under nitrogen atmosphere for a defined period of time. Several experimental parameters of the process were investigated to determine the optimum conditions. The effects of heating temperature, heating time and particle size of PVC waste on the emitted vapors are studied. Set of experiments are carried out by changing the temperature (200, 250, 275, 300 and 325 °C) and heating times (7.5 to 60 min) at each temperature. The amount of hydrogen chloride (HCl) gas evolved at each temperature is trapped in 0.3 M sodium hydroxide solution and measured by titrating against 0.2 M HCl solution.

PVC waste granules are grounded further to grain sizes of 0.5, 1.0, and 2.0 mm and sieved out in order to study the effect of particle size. Exactly 5.0 g of each grain size was pyrolysis at optimum temperature to release of the maximum amount of HCl before organic fumes liberated. The amount of HCl evolved was calculated and heating time before organic fumes liberation was recorded for each experiment.

### *C. Collection of HCl*

These experiments were conducted by using the most determined previously suitable conditions for PVC pyrolysis (optimum temperature, heating time and grain size). The experiment was repeated using the two HCl traps in sequence, the first contained 100 ml and the second 500 ml distilled water. The experiment was repeated several times until the first trap was saturated with HCl. The HCl concentration in the two traps was determined after the degradation of 100.0 g PVC samples (each sample 10.0 g). A sample of HCl solution is used to determine its concentration by titration method against 0.4 M NaOH using phenolphthalein indicator.

The experiment was repeated to investigate the purity of the collected HCl. The HCl trap contained an equivalent amount of NaOH solution (500 ml) reacted the emitted HCl from 15.0 g PVC waste. The final solution was transferred to a 1000 ml beaker and evaporated to dryness. Finally, the purity of the produced salt was analyzed by using CHNS elemental analyzer (Euro Ea Elemental Analyzer).

### *D. Extraction and Collection of Organic Materials*

These experiments were performed on the black solid material remained after HCl evolution for the purpose of converting it into carbon black. The pyrolysis setup was assembled with collection flask to collect the produced organic materials. In this process, the temperature was raised to 400 °C for 2.0 hr during which all the organic material was formed and evaporated, Amount of evolved organics and black carbon remains were determined by weighting of starting and final solid materials.

### *E. Extraction of Black Carbon and Organic Metals Content*

Heavy metal compounds are normally used as additives in

manufacturing process of PVC pipes as coloring agent. Therefore, the carbon black from pyrolysis process must contain heavy metal ions. These metals may be removed to have a clean black carbon as end product. To remove the ions, a sample of black carbon was grounded to fine particle sizes using a Ball Miller. About 20 ml of concentrated nitric acid was added to a 1.0 g sample in a glass beaker and the mixture heated to near dryness. This step repeated twice, distilled water was then added and the mixture filtered into a 50.0 ml volumetric flask. The volume completed to the mark and concentration of Zn, Cu, Pb, Cd, Co and Fe were determined using Atomic Absorption Spectrophotometer (Alpha 4 Atomic Absorption Spectrophotometer).

A sample of PVC resin was pyrolysis in the same way as the PVC waste. Exactly, 1.0 g carbon black from this sample was grounded, HNO<sub>3</sub> digested and the heavy metal content was determined and used as a reference sample.

The presence of heavy metal ions in the organic distillate was also investigated by treating 0.5 g sample by 10.0 ml concentrated HNO<sub>3</sub> in a beaker and heated to near dryness. After that, 5.0 ml of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) was added and the mixture boiled for 3 min. The final mixture was filtered into 50.0 ml volumetric flask and the heavy metals content was also measured.

## III. RESULTS AND DISCUSSION

Hydrogen chloride is one of the main degradation products in the pyrolysis process of polyvinyl chloride. The presence of air in the process leads to the formation of carbon monoxide and carbon dioxide beside other organic products. To collect hydrogen chloride and maintain high yield of carbon black, a set of thermal degradation experiments were performed to PVC under inert atmosphere at different temperatures ranged from 200 °C to 325 °C for various time intervals for each processing temperature. Figure 1 shows the dehydrochlorination of PVC at various temperatures as a function of heating time. It can be seen that the percentage of the emitted HCl increases when the PVC particles heated at 200 °C up to 45 min at constant temperature. Only about 23% of the theoretical pre-calculated HCl is released even up to 90 min without any observed organic vapors.

Since the thermal degradation reactions proceed with significant activation energies then the temperature has an important effect on the rate. In the same way, dechlorination of polyvinyl chloride waste at 250 °C and different period of times was also investigated. There is slight difference in the trend of HCl evolution. About 30% of HCl is emitted in the first stages during 15 min of heating. Further increase of the heating time led to slow rate of release with the total of about 52% during 150 min heating time without any observation of organic fumes.

It is very obvious that the emission of HCl reaches 40% during only 7.5 min, 48% and 80% in 15 min and 60 min heating time respectively, when the waste was heated at 275 °C. Insignificant effect of heating time on release of HCl was detected when heating time was continued up to 90 min. At 300 °C, the release of HCl is more effective than 275 °C degradation temperature by as much as 25% in the first stages (15 min). In addition, the yellow organic fumes are observed

after 22 min degradation time.

Fig. 1 also shows the plot of degradation time of PVC waste versus %HCl released under nitrogen atmosphere at 325 °C. When the waste heated for 11 min the percentage of HCl reaches to about 72% and yellow organic vapors are observed. The results indicate that the degradation temperature plays an important role in the overall release of hydrogen chloride. Almost complete release of HCl gas was at 300 °C and this seems to be the optimum temperature for the removal of chlorine from the PVC waste. The sharp increase in the HCl release in the first stages for all processing temperatures could be due to the dechlorination of the outer layers of the PVC waste particles resulted from direct contact with heat. Further heating time led to relative slow release. That may be attributed to the formation of thermal crosslinking of the chains which could result in a dense matrix and prevent the dechlorination process. As a result, high temperature is needed to complete the degradation process and emission of the rest of HCl and other organic products.

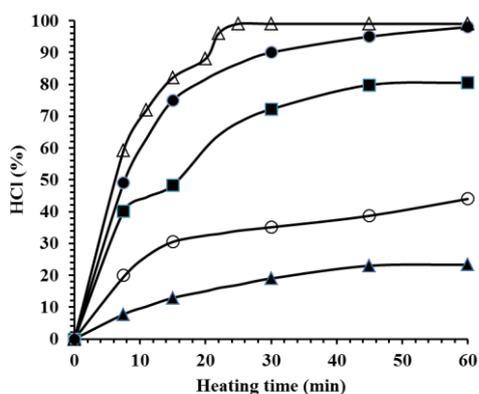


Fig. 1. Effect of degradation time of PVC waste of particle size ranged from 0.5-4 mm on the release of HCl at various temperatures [▲: 200 °C, ○: 250 °C, ■: 275 °C, ●: 300 °C, △: 325 °C].

The thermal degradation does not depend on initial amount of polymer but the rate of degradation process may depend on the particle size of the waste. For this reason, the rigid PVC waste samples of different particle sizes (0.5, 1.0 and 2.0 mm diameters) are subjected to thermal degradation at 300 °C. Fig. 2 represents the percentage of HCl released versus heating time at 300 °C for a particle size of 0.5 mm. It is very clear that most of HCl (88%) was released during 10 min of the degradation process. The organic vapors started to appear at 16.5 min while about 95% of HCl was released.

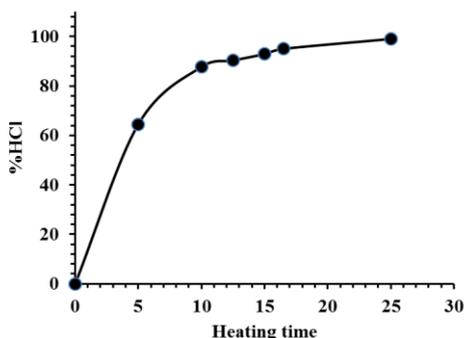


Fig. 2. Effect of degradation time of PVC waste of 0.5 mm particle size on the release of HCl at 300 °C.

Table I presents the relationship between the particle sizes, degradation temperature, percentage of hydrogen chloride released and recorded time of starting of yellow organic vapors emission. A significant effect of particle size on both the percentage of HCl and time of emission of organic vapors are observed. It is noticeable that the smaller the particle sizes the higher the rate of dichlorination and the rapid the formation of organic compounds. That could be attributed to (1) increase of surface areas in contact with heat and (2) disability of small particle to retain the HCl gas and organics in the last stages of the decomposition.

TABLE I: THE RELATIONSHIP BETWEEN THE PARTICLE SIZES, DEGRADATION TEMPERATURE, PERCENTAGE OF HYDROGEN CHLORIDE RELEASED AND TIME OF STARTED YELLOW ORGANIC VAPORS EMISSION

Particle size (mm)	Heating temperature (°C)	HCl (%)	Time of organics evolved (min)
0.5	300	95	16.5
1.0	300	93.20	18.0
2.0	300	92.00	21.0
0.5-4.0	300	90.00	22.0
0.5-4.0	325	71.99	11.0

Fig. 3 presents the obtained concentration of HCl solution resulted from the thermal degradation of PVC waste in both traps at 300 °C and 16 min heating time. It is very clear that most of the emitted HCl was collected in the first trap due to the very high solubility of the gas in distilled water forming highly concentrated hydrochloric acid solution. The maximum concentration of HCl solution obtained under these experimental conditions was 11.2 M which is nearly the same as the concentration of commercial laboratory grade hydrochloric acid. Generally, the weight of both the released HCl and the residual material from the thermal degradation represent most of the original weight of the PVC samples. To investigate the purity of the achieved acid solution, sodium chloride salt was prepared and analyzed by CHNS. The results showed that the concentration of carbon and hydrogen were under the detection limit of the instrument. It revealed that the hydrochloric acid is free of any organics.

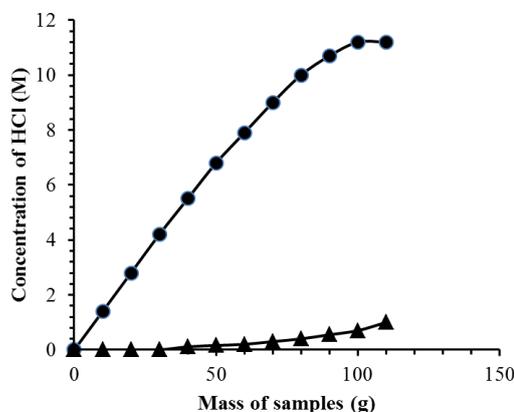


Fig. 3. Molar concentration of the collected hydrochloric acid [●: first trap, ▲: second trap].

The residual materials from the previous experiments are subjected to higher temperature to complete its thermal degradation in order to be converted to organic compounds

and carbon black powder. The percentage of the obtained carbon powder was about 27% of the PVC waste. The concentration of the extractable heavy metals in carbon powder, virgin PVC as a reference sample and organics were analyzed and the data is presented in Table II. Available Pb has the highest concentration in the produced carbon black from PVC waste and unavailable in both virgin PVC and organics. The presence of high concentration of Pb in the carbon powder ( $37.43 \text{ mg.g}^{-1}$ ) was due to the addition of lead organic compounds as additives during the PVC processing. The small concentration of Zn and Fe in carbon powder and virgin PVC may be due to contact of PVC with metal surfaces of equipment during production and processing steps. The concentrations of heavy elements in organic compounds were under the detection limit. In addition, about 14% of initial weight was found to be as heavy metals free oil and that could be used as fuel.

TABLE II: CONCENTRATION OF HEAVY METALS IN CARBON BLACK POWDER AND ORGANIC COMPOUNDS

Metal	Black Carbon ( $\text{mg.g}^{-1}$ )	Virgin PVC ( $\text{mg.g}^{-1}$ )	Organic Compounds ( $\text{mg.g}^{-1}$ )
Pb	37.43	*	*
Zn	$34.08 \times 10^{-3}$	$1.69 \times 10^{-3}$	*
Fe	0.42	$10.20 \times 10^{-3}$	*
Cd	*	*	*
Cu	*	*	*
Co	*	*	*

\*: Under Detection Limit.

#### IV. CONCLUSION

The study of PVC waste degradation under controlled inert conditions revealed that the dehydrochlorination was dependent on temperature, heating time and grain size. It was increased with raising temperature and the optimum dehydrochlorination temperature was  $300 \text{ }^\circ\text{C}$ . Furthermore, the rate dechlorination and HCl formation was increased with heating time but decreased when particle size increased. The highest percentage of HCl (95%) liberated when the sample of 0.5 mm grain size was heated at  $300 \text{ }^\circ\text{C}$  for 16 min before any observation of yellow organic fumes. The maximum concentration of hydrochloric acid solution prepared from this experiment was 11.22 M without any detected hydrocarbon or heavy metals contamination.

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