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Eco Friendly-Recycling Of Waste PET Bottles Via Recovery Of Terephthalic Acid (TPA) Using Amberlite IR-120[H^+] Resin As A Reusable Catalyst.

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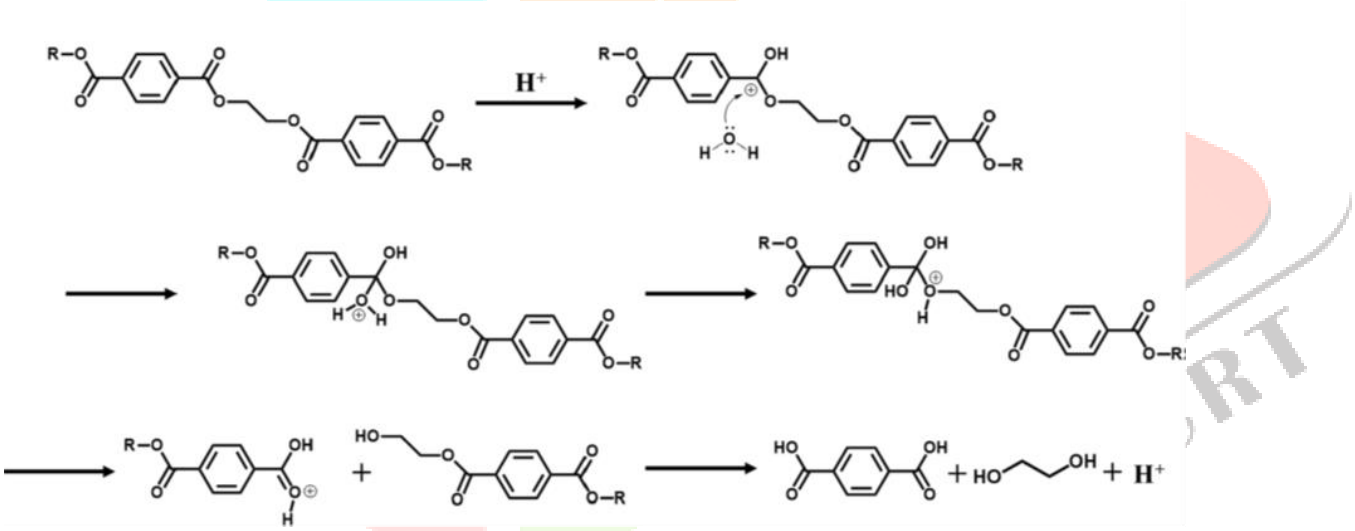
Abstract:

The recovery of plastic waste plays a crucial role in improving waste management by giving discarded plastics a new purpose. An effective method for recovering plastic waste is hydrolysis treatment, where the plastic monomers are recovered through depolymerization. This study specifically examines the recovery of polyethylene terephthalate (PET) using solid acid-mediated or catalyzed synthesis. The analysis focuses on the weight changes of PET under different hydrolysis conditions, including various reaction times and temperatures. Additionally, the study evaluates the recovery of the PET monomer, referred to as terephthalic acid (TPA). The results indicate that higher temperatures with different catalysts such as the green catalyst Amberlite IR-120[H^+] resin or $NiCl_2$, and longer reaction times contribute to higher TPA recovery. The measured PET residue, reflected in weight differences, aligns with the observed trend in TPA yield. Particularly, hydrolysis with an acidic catalyst under milder conditions proves to be more efficient in recovering TPA compared to harsh basic or strongly acidic conditions. The knowledge gained from this study holds significant potential for upcycling plastic waste into valuable end products. By understanding the optimal conditions for TPA recovery from PET, this research provides valuable insights into maximizing the effectiveness of hydrolysis processes. Ultimately, these findings contribute to the development of sustainable processes for converting plastic waste into high-value resources.

Keywords: Hydrolysis; Plastic Waste; Polyethylene Terephthalate (PET); Terephthalic Acid (TPA); Amberlite IR-120[H^+] resin, $NiCl_2$, Waste Recovery, Depolymerisation.

Statement of the Problem:

The disposal of plastic waste has become a significant environmental problem that requires effective solutions for its management and sustainable use. Despite the increasing importance of recycling, there is still a need to explore advanced methods for the recovery of plastics, especially for polyethylene terephthalate (PET). Hydrolysis treatment, especially by depolymerization with Amberlite IR-120[H^+] resin or Lewis's acid such as $NiCl_2$, in polar solvents at moderate temperatures is a promising way to recover PET (Scheme-1). However, there is a lack of comprehensive understanding of the optimal conditions for this hydrolysis process. The current state of knowledge lacks detailed insights into the influence of different reaction times and temperatures on the weight changes in PET and the subsequent recovery of the valuable monomer terephthalic acid (TPA). Furthermore, a comparative analysis of the efficiency of Amberlite IR-120[H^+] resin and NiCl2 catalyst in PET recovery is essential.

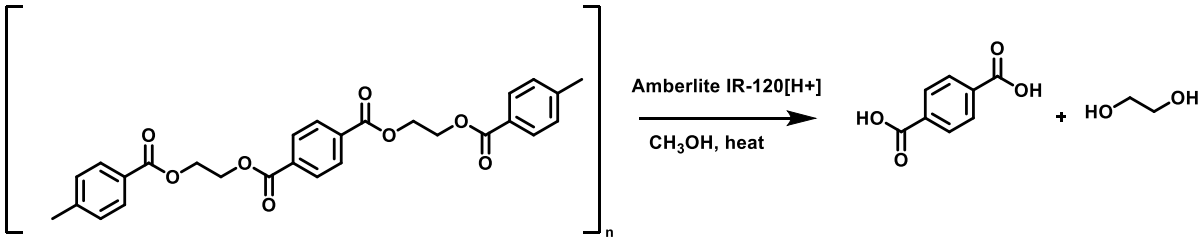


Scheme 1: PET hydrolysis mechanism with TPA as an acid catalyst.

Hypothesis:

We hypothesize that the recovery of polyethylene terephthalate (PET) by hydrolysis treatment with Amberlite IR-120[H^+] resin or $NiCl_2$ will be affected by different reaction times and temperatures (Scheme). We hypothesize that higher temperatures and longer reaction times will lead to increased recovery of the monomer terephthalic acid (TPA) from PET. We predict a positive correlation between these variables, suggesting that optimal conditions for PET recovery can be achieved by careful manipulation of hydrolysis parameters.

Furthermore, we propose that hydrolysis with Amberlite IR-120[H^+] resin will outperform $NiCl_2$ hydrolysis in terms of TPA yield and catalyst recovery. It is expected that the chemical properties of Amberlite IR-120[H^+] resin will improve the depolymerization of PET, leading to a more efficient recovery of the valuable monomer. This hypothesis is based on the understanding of the reactivity of Amberlite IR-120[H^+] resin with PET compared to $NiCl_2$. By testing these hypotheses, we aim to gain valuable insights into the factors influencing PET recovery during hydrolysis and contribute to the development of optimized methods for the conversion of plastic waste into high-value end products. These findings have the potential to support sustainable practices in plastic waste management and facilitate the transition to a circular and environmentally friendly approach to plastic recycling.



Scheme2: Synthesis of terephthalic acid (TPA) from PET

Aims:

The present study aims to fill these gaps by systematically investigating the effects of different hydrolysis conditions on PET recovery, with a focus on TPA yield. The comparison between Amberlite IR-120[H^+] resin and Lewis's acid such as $NiCl_2$ catalyst will provide crucial insights into the effectiveness of different catalysed hydrolysis agents under boiling polar solvent conditions. The results of this research will contribute to the development of sustainable processes for the upcycling of PET plastic waste, reducing the environmental impact associated with plastic disposal.

Objectives:

- **Investigate Hydrolysis as a Plastic Waste Recovery Method**: Investigating the potential of hydrolysis treatment as an effective approach to recovering plastic waste, with a particular focus on polyethylene terephthalate (PET). Evaluate the contribution to solid waste management and the possibility of giving new life to discarded plastics.
- **Explore Recovery of PET with Amberlite IR-120[H^+] or $NiCl_2$ catalyst:** Investigation of PET plastic recovery by hydrolysis treatment with two different agents such as Amberlite IR-120[H^+] resin, $NiCl_2$. Evaluation of the efficiency and effectiveness of each hydrolysis solution in the recovery of plastic monomers through the depolymerization process.
- **Analyse Weight Changes in PET:** Systematic analysis and quantification of the weight changes of PET when exposed to different hydrolysis agents, reaction times and temperatures. The aim is to understand how these variables affect the physical properties of PET during the recovery process.
- **Evaluate Monomer Recovery (TPA) from PET:** Evaluate the recovery of the monomer from PET, in particular terephthalic acid (TPA). Investigate how different hydrolysis conditions affect the yield of TPA and gain insight into the optimal parameters to maximize monomer recovery.
- **Examine the Influence of Reaction Times and Temperatures:** Investigation of the effects of different reaction times and temperatures on the recovery of TPA from PET. Analyse the trends and correlations between these variables to identify the conditions that promote high monomer recovery.
- **Compare Amberlite IR-120[H^+] resin and $NiCl_2$ catalyst reaction conditions:** Conduct a comparative analysis between Amberlite IR-120[H^+] resin and $NiCl_2$ as hydrolyzing agents. Evaluate their respective abilities to recover TPA from PET to gain insight into the relative effectiveness of these systems in upcycling plastic waste.

- **Correlate PET Residue with TPA Yield:** To establish a correlation between the measured PET residue (weight difference) and the corresponding TPA yield. The aim is to validate the relationship between the observed changes in PET mass and the success of the depolymerization process.
- **Provide Knowledge for Upcycling Plastic Waste:** To summarize and disseminate the knowledge gained from the study to gain valuable insights into the upcycling of plastic waste into high-quality end products. This objective aims to support the development of sustainable practices in the plastic waste industry based on empirical evidence.

Review of Literature:

Plastic waste has become a global environmental problem, which has led to extensive research into new ways for its recovery and long-term management. This study looks at the national and international literature to provide an overview of the current state of research on plastic waste recovery, with a focus on polyethylene terephthalate (PET) and hydrolysis treatment.

Geyer and colleagues (2017). Production, use, and disposal of all plastics ever created. Science Progresses, this major international study provides an in-depth examination of global plastics production, consumption and fate in the environment. It emphasizes the crucial importance of appropriate systems for the disposal of plastic waste. Achilias and Karayannidis (2004) state. Hydrolysis of poly(ethylene terephthalate) in the molten state. Polymer, This global study examines the hydrolysis of PET in the molten state and provides insights into the chemical mechanisms involved. The work provides useful information on the depolymerization of PET, which is an important part of plastic waste recycling. The occurrence of microplastics in the marine environment. Marine pollution by A. L. Andrady (2011).

While not directly related to hydrolysis, this international study raises awareness of the global problem of microplastics and highlights the importance of sustainable plastic waste management practices. Jambeck and colleagues (2015). Plastic waste from land ends up in the sea. Published in the journal Science, this nationwide study examines the import of plastic waste into the ocean, highlighting the importance of land-based sources. It emphasizes the importance of appropriate waste recycling systems, particularly hydrolysis processes, to reduce marine pollution. According to Salem et.al,(2010). A overview of the recycling and recovery routes for plastic solid waste (PSW). Management of Waste, This nationwide assessment, which focuses on solid plastic waste, examines alternative recycling and recovery strategies, including hydrolysis. The work sheds light on the feasibility of hydrolysis as a method of PET recovery. Plastic waste to liquid gasoline by hydrolysis: An overview. Das et al. (2018), Materials Today: Proceedings.

This national assessment looks at the hydrolysis of waste polymers to produce liquid fuel and offers insights into the wider applications of hydrolysis in plastic waste management. Worldwide literature highlights the global scale of the plastic waste dilemma, while national research offers insights into specific areas of plastic waste recycling, such as hydrolysis. The cited publications contribute to the growing body of knowledge aimed at developing sustainable practices for plastic waste management. Amberlite IR-120[H^+] resin is an efficient catalyst for chemical transformations such as condensation reactions and has attracted considerable attention due to its recyclability (Sharma et al., 2009). $NiCl_2$ is a Lewis acid catalyst that can also be useful for the saponification reaction Khan et al. (2003).

Material and Methods:

PET bottles discovered in a garbage vicinity near Govt Degree College Siddipet were selectively gathered, emphasizing the collection of only clear PET bottles to maintain material consistency. In preparation for their use in experiments, a meticulous cleaning process was implemented. The PET bottles underwent a thorough rinse with distilled water, followed by an air-drying procedure.

Subsequently, the PET bottles were precisely cut into small, identical pieces, each measuring 1cm by 1cm, using scissors (Figure 1). This cutting process was executed with precision, ensuring that the selected region for cutting remained flat. This precautionary measure was taken to guarantee a uniform surface area for all samples, thereby promoting consistent conditions for the hydrolysis reaction.

To further eliminate any potential impurities, the cut PET bottle pieces underwent an additional rinsing step, this time utilizing deionized water. Following this rinse, the samples were allowed to dry at room temperature once more. This sequential cleaning and drying process was meticulously carried out to uphold a standardized approach in the preparation of the PET samples for subsequent hydrolysis experiments.

This methodical procedure, from the careful selection of clear PET bottles to the precise cutting and thorough cleaning processes, ensures that the hydrolysis reactions take place on PET samples with uniform characteristics. This consistency is vital for the reliability and accuracy of the experimental results, enabling a meaningful analysis of PET hydrolysis under controlled conditions.







Clear PET bottles were selectively collected from the garbage vicinity near Govt Degree College Siddipet, focusing on maintaining material consistency. These bottles will be utilized for experiments in the Chemistry Department laboratory at GDC Siddipet.

Figure 1: PET Bottles

Figure 2: Collection of plastic pieces.

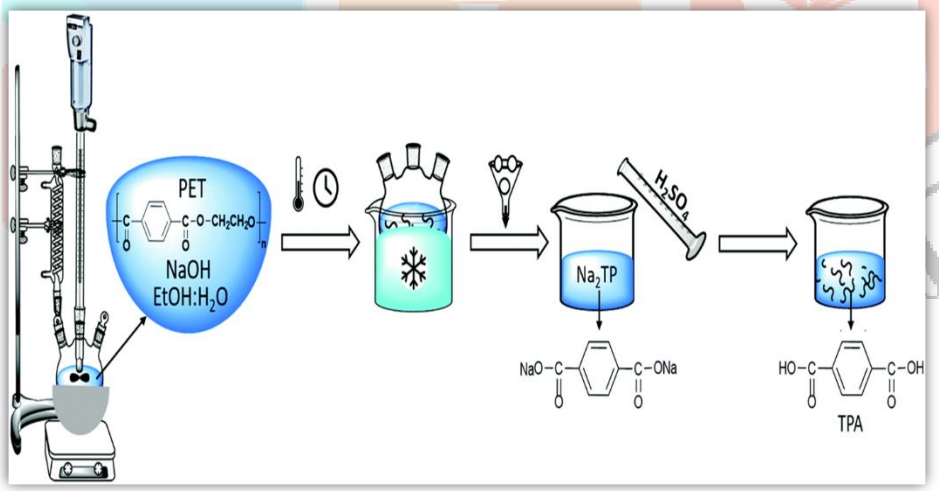


Fig- 3 Recycling of multilayer and colored pet plastic waste by alkaline hydrolysis

Two different hydrolysis agents, Amberlite IR-120[H^+] resin and $NiCl_2$ were employed in the hydrolysis process. The experiment began with 5 grams of sliced PET plastic being accurately weighed before immersion in 50 mL of methanol or ethylene glycol 10-20 equivalent of each catalyst will be used. This procedure will be conducted in individual reaction setups. Subsequently, the reaction setups were placed in a reactor and subjected to specific temperatures of 40°C and 65°C, respectively. This experimental setup was adapted from the methodology outlined by Hanaoka *et al.* in 2021.

The part was to determine the optimal depolymerization parameters that would allow the production of the highest yield of TPA and EG (ethylene glycol). The following parameters optimized were the catalyst used and reaction time. Then, the TPA obtained were characterized together with their corresponding standards using Fourier transform-infrared spectroscopy (FT-IR). Due to limited isolation facilities, we could manage the isolation of TPA without traces of EG.

Results and Discussion

Effect of Temperature in Weight Different and TPA Yield of PET Plastic

In the depolymerization of waste PET to produce TPA, two parameters were optimized, namely the catalyst used (Amberlite IR-120[H^+] resin, $NiCl_2.6H_2O$) and the reaction time. For the general procedure, 1 g of PET flakes, 50.00 mL methanol or EG were weighed in analytical balance or measured using volumetric pipets and placed into a 250 mL round-bottom distilling flask. An amount of 3 g of the catalyst to be optimized was also added to the flask. The flask was then equipped with a Claisen head, a reflux condenser, a thermometer, and a magnetic stirrer. The mixture was heated up to its boiling point with constant agitation using an oil bath placed in a magnetic-stirring hot plate. A reflux condenser was placed to avoid the loss of volatile products and reagents in the reaction as much as possible. The reaction time was then optimized. We further investigate the parameters to be optimized (Table 1). For the TPA, at the end of each run, the heat source was removed, and the mixture obtained was filtered to separate the unreacted PET residue from the catalyst. The residue was then washed with distilled water, dried at 105 °C for 4 h, cooled, and weighed. Dilute hydrochloric acid (1 M) was added dropwise to the filtrate obtained with constant stirring to form the white precipitate, TPA. Afterward, the TPA was digested at 70 °C for 30 min to increase particle size, cooled, and then filtered. The TPA solid was washed using distilled water to remove water-soluble impurities, filtered again, dried at 105 °C, and then finally weighed, and stored in a clean container. (Fig. 3) shows the schematic diagram for the isolation of TPA. Fig. 4 shows the correlated FT-IR of TPA generated from depolymerization with reference TPA. Fig. 5 shows the correlated 1HNMR of TPA generated from depolymerization with reference TPA. We further checked optimum heating studies with different catalysts, and we found the TPA yields were improved with reflux temperatures with 24hrs reaction time (Table-1). We also recovered catalyst along with PET traces which can be re-used up to four cycles, we see barely any difference in the isolated yields. A similar reaction condition was applied using a $NiCl_2.6H_20$ catalyst and in this case catalyst was not recovered. We also conducted a similar experiment in EG as solvent at its boiling temperatures and we found improved yields with TPA synthesis.

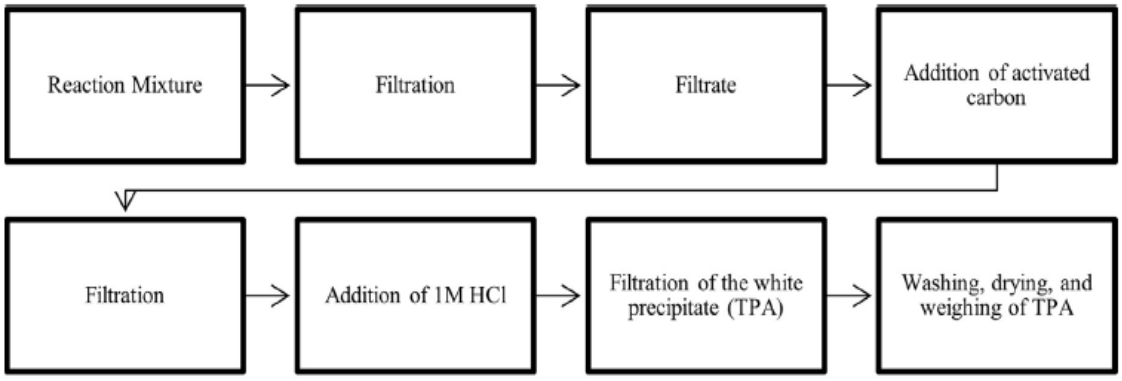


Figure -4: Isolation of TPA

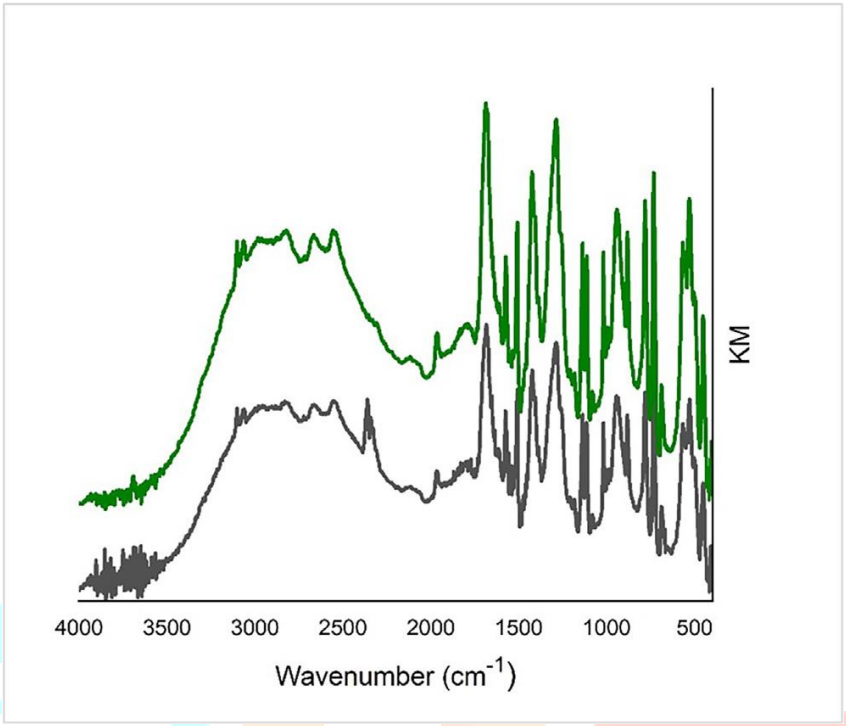


Figure 5: FT-IR spectra of (a) TPA product in black and (b) TPA standard in green.

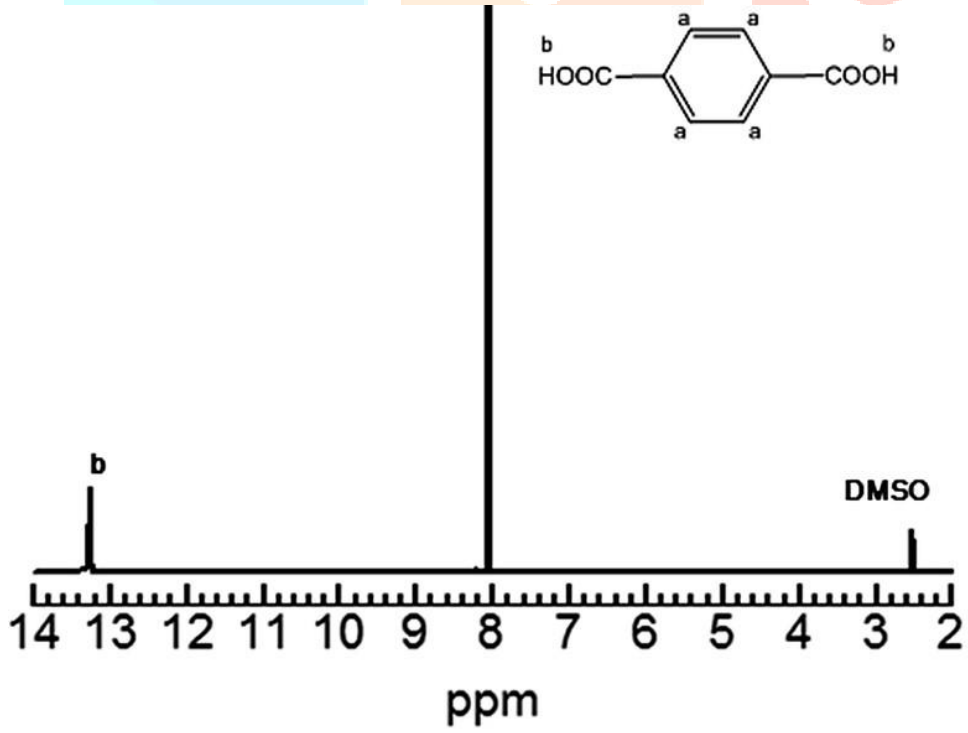


Figure 6: ^{1}HNMR of terephthalic acid (TPA) in DMSO-d_6

Table: Parameters to be optimized for TPA recovery

Entry	Catalyst	Solvent	Temp ºC	Reaction Time, hrs	Yield, %
1	Amberlite IR-120[H^+] resin	CH_3OH	65	24	20
2	Amberlite IR-120[H^+] resin	CH_3OH	65	48	22
3	Amberlite IR-120[H^+] resin	EG	180	24	72
4	$NiCl_2.6H_2O$	EG	180	24	74
5	$NiCl_2.6H_2O$	EG	180	48	81

Conclusion:

Hydrolysis is proving to be a promising technology for the recovery of monomers from plastic waste through efficient degradation in the depolymerization process. Recent studies show that mild and safe acid-mediated or catalyzed hydrolysis outperforms the recovery of terephthalic acid (TPA), a key monomer in polyethylene terephthalate (PET). Furthermore, the efficiency of TPA recovery was found to be influenced by the choice of hydrolysis solution or catalyst. In particular, the resin Amberlite IR-120[H^+] can show improved TPA recovery which is comparable to $NiCl_2$. However, it is crucial to recognize the significant advantages and effectiveness of $NiCl_2$ in monomer recovery from PET. Percentage recoveries are influenced by several factors, including high temperatures, long reaction times, and the nature of the reactant. These parameters play a crucial role in determining the efficiency of recovering valuable monomers from plastic waste. While previous research shows the importance of temperature and the choice of hydrolysis solution, further investigation is strongly recommended. Future studies should investigate the inclusion of different plastic loadings, variations in pH, and the use of enzymes to increase product recovery rates. In addition, recovery performance using different acid types should be investigated to fully understand their effects on monomer recovery efficiency.

To summarize, although mild acid hydrolysis is a promising route for the recovery of monomers from plastic waste, there is still room for further research and refinement. The optimization of conditions, research into different reactants, and a comprehensive understanding of the underlying mechanisms will contribute to the development of more efficient and sustainable processes for recovering valuable monomers from plastic waste.

References:

Achilias, D. S., & Karayannidis, G. P. (2004). Hydrolysis of poly(ethylene terephthalate) in the molten state. Polymer, 45(12), 4111-4116.

Al-Salem, S. M., Lettieri, P., & Baeyens, J. (2010). Recycling and recovery routes of plastic solid waste (PSW): A review. Waste Management, 30(11), 1934-1950.

Cˇolnik M, Knez Z and Škerget M 2021 Sub- and supercritical water for chemical recycling of polyethylene terephthalate waste Chemical Engineering Science 233 Article 116389

Das, B., Sarkar, D., Deka, D., & Baruah, D. C. (2018). Waste plastics to liquid fuel through hydrolysis: An insight review. Materials Today: Proceedings, 5(1), 2390-2395.

Geyer, R., Jambeck, J. R., & Law, K. L. (2017). Production, use, and fate of all plastics ever made. Science Advances, 3(7), e1700782.

Hanaoka T, Arao Y, Kayaki Y and Kuwata S 2021 Analysis of nitric acid decomposition of epoxy resin network structures for chemical recycling Polymer Degradation and Stability 186 Article 109537

Jambeck, J. R., Geyer, R., Wilcox, C., Siegler, T. R., Perryman, M., Andrady, A., ... & Law, K. L. (2015). Plastic waste inputs from land into the ocean. Science, 347(6223), 768-771.

Khan, A. T., Mondal, E., Sahu, P. R., & Islam, S. (2003). Nickel (II) chloride as an efficient and useful catalyst for chemo-selective thio acetalization of aldehydes. *Tetrahedron letters*, *44*(5), 919-922.

Yang W, Liu R, Li C, Song Y and Hu C 2021 Hydrolysis of waste polyethylene terephthalate catalyzed by easily recyclable terephthalic acid Waste Management 135 267–274

Sharma S D, Konwar D. Synth Commun, 2009, 39: 980.