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Original Article

High-Quality Synthesis of Terephthalamide from Secondary PET Waste

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***Abstract* - *The article studies the two-step process of Terephthalamide synthesis, which is used to produce various polymers, pigments, and antioxidants. In the production of Terephthalamide, the relevant raw material, terephthalic acid, was synthesized from PET waste using a high-yield reaction method. Terephthalamide was synthesized from the obtained terephthalic acid. The effect of pressure, mass ratio of starting materials, temperature, and catalyst was studied to increase the reaction yield. Graphs and diagrams were constructed according to the reaction results. At the same time, the IR spectrum and Raman spectrum of the obtained Terephthalamide were obtained and analyzed. Also, the molecular structure, dynamics of intermolecular interactions, and thermal properties were studied using NMR analysis, TGA, and DTA analysis methods. Based on the results of the analysis, it was proven that the product obtained was terephthaldiamide.*

***Keywords* - *Polyethylene terephthalate (PET), Glycerin, Ethylene glycol, Urea, Reactor autoclave, Reaction product, Amination, Terephthalamide, DEF, DMSO.*

1. Introduction

Waste polyethylene terephthalate (PET) will be the main topic of discussion. Discarded PET has grown to be a major environmental issue globally due to issues including inadequate handling, lack of infrastructure, and low civic awareness [1]. Of the 8.3 billion non-biodegradable plastic products generated globally since the 1950s, just 11% are recycled. Global polymer production in 2021 was 390.7 million tons, an 8% rise over last year [2]. Of this, polyethylene terephthalate (PET) manufacturing [3] accounted for 8%. Excellent PET qualities include minimal thermal expansion, chemical resistance, and good strength [4]. These qualities make PET valuable in many other fields, including food packaging, textiles, and various beverage containers [5]. A vital substance widely utilized because of its exceptional physical and chemical qualities is polyethylene terephthalate, also known as PET in the packaging sector and "polyester" in the textile industry [6-7].

However, because PET is becoming more and more popular and is not biodegradable, disposing of it has led to significant environmental and financial issues [8]. Consequently, handling PET trash has emerged as a significant social concern. Recycling PET waste is still the best choice because of society's growing environmental consciousness [9]. Since chemical recycling creates raw materials, it is the only PET recycling technique that adheres to sustainable development principles [10–16]. Processes like hydrolysis, methanolysis, glycolysis, ammonolysis, and aminolysis are used in chemical recycling [11-17]. Increasing the monomer yield, reducing reaction time, and conducting the reaction under favorable circumstances are the primary goals of the substantial study on PET chemical recycling [12-17]. Numerous chemical processing procedures have been developed as a result of ongoing research efforts [13-18]. Nowadays, PET waste is used in various industries through recycling. Many materials in the construction industry are also produced by recycling PET, such as various tiles and corners. For this, the collected PET waste is collected, thoroughly cleaned, and then crushed. Then it is mixed with various plastics, melted, and poured into molds. Such construction and decoration materials are considered very durable. This is one of the simple and effective ways to use PET waste[14].

Many products are obtained by chemical processing. PET is mainly synthesized using terephthalic acid and ethylene glycol. Therefore, when processed by chemical methods, these two substances are obtained. More attention is paid to terephthalic acid than to ethylene glycol. Many substances necessary for the chemical industry are obtained from terephthalic acid. They are widely used as raw materials in producing polymers and various organic solvents (for example, benzene dichlorobenzene) [15]. There are many methods for obtaining terephthalamide from terephthalic acid.

These include amination of terephthalic acid with copper salts, decomposition of PET waste with monoethanolamine, separation of the resulting compound by recycling, and other similar methods. However, all of these have various problems, such as the purity of the resulting product, the multi-step nature of the process, and the low reaction efficiency. These shortcomings remain major problems that need to be addressed [16].

At the same time, there is an effective method for obtaining terephthaldiamide by converting terephthalic acid obtained from the chemical processing of polyethylene terephthalate into an oligomer with ethylene glycol and passing ammonia gas under high pressure. The only major drawback of this method is that it requires a very long time for each reaction step (an average of 10-12 hours for each step), and by-products are formed that are difficult to separate from the final product. The shortcomings of this and other methods have been studied, and a method has been developed that has a shorter reaction time, limited formation of by-products that are difficult to purify, and high reaction efficiency.

2. Experimental Part

2.1. Materials and Methods

Clean and crushed pieces of PET bottles and articles were used to conduct the study. Urea, sodium hydroxide, glycerin, ethylene glycol, a high-altitude reactor autoclave made of ordinary stainless steel of the HNXIB brand with a volume of 5 L.

2.2. Synthesis of Terephthalic Acid

We perform the decomposition of PET with an alkaline solution. The disadvantage of this method is the time and temperature [14]. Because the reaction requires a high temperature for a long time [15]. To carry out the reaction, 500 ml of heat-resistant glass, 60 g of PET pieces, 120 g of alkali and 180 g of water are required. First, a solution of alkali and water is prepared and poured into a glass, and PET pieces are added and heated. It is heated to 120-150 ° C, and the reaction proceeds with boiling. The reaction lasts 3 hours [16]. At the end of the reaction, the PET pieces are completely decomposed, and a thick white solution is formed. In the next step, ethylene glycol and the sodium salt of terephthalic acid, placed in a 2-3 liter container, are dissolved in 1-1.5 liters of water, and a colorless solution is obtained. This solution is neutralized with sulfuric or hydrochloric acid, and pure terephthalic acid is obtained. Since the reaction is very fast, a white colloidal solution is formed as a result of foaming when acid is added. It is filtered to separate the terephthalic acid, and the obtained terephthalic acid is washed again to remove sodium salts. The advantage of this method is that it is possible to obtain high-quality terephthalic acid.

2.3. Synthesis of Terephthalamide

The reaction to obtain terephthalamide is carried out with a mixture of terephthalic acid and urea at a pressure of 5-6 atm at a temperature of 185 ° C. First, we need a reactor autoclave. 50 g of urea and 72 g of terephthalic acid are placed. The volume of the reactor autoclave should be 5 L. The reaction lasts 3 hours. After the pressure initially exceeds 100 ° C, the pressure begins to rise. When it reaches a pressure of 6 atm, the gas is released by opening the gas outlet to stop the pressure increase, and in this state, it is controlled to be in equilibrium pressure. After 4 hours, when the urea is completely decomposed into carbon dioxide and ammonia, and a certain part of the ammonia formed reacts with terephthalic acid, the pressure gradually decreases. At this time, the reactor autoclave can be turned off, waiting for a pressure drop of 3 atm. The resulting product is washed in water at 90°C. This removes the biuret and isocyanides formed during the reaction. After filtration, it is dried, and terephthalamide is obtained with a yield of 60-65%.

If inorganic salts are used as catalysts in the reaction, the reaction yield can be increased to 70-75%. Terephthalamide is practically insoluble in most solvents. It is soluble only in DEF and DMSO, at 6 g per 100 ml. It is also soluble in alkaline solutions, but sodium reacts with it to form water-soluble organic salts and releases ammonia gas. In order to obtain high yields in the reaction process, we need to pay attention to the mass ratios of the starting materials.

In Figure 1, different mass ratios of terephthalic acid and urea are shown in the diagram with the reaction yields. From this diagram, we can see that the mass ratio of terephthalic acid and urea with the highest yield is 1:1.4. After selecting a mass ratio with a high reaction yield, and the reactions were carried out as a function of pressure, temperature, and time. For example, the graph in Figure 2 shows the results of studying the effect of temperature on the reaction at the selected mass ratio.This graph shows that the reaction yield increases with increasing temperature, and the highest yield is obtained at 185 °C, which decreases from 195 °C onwards. This is because, at higher temperatures, terephthalic acid also starts to decompose. Based on the reaction yields related to pressure, time and catalyst, the diagrams in Figure 3, Figure 4 and Figure 5 were constructed, and the mass ratio of terephthalic acid and urea in the reactions was taken as 1:1.4. In Figure 3, the highest yield is observed at a pressure of 6 atm.

As the pressure increases, the reactivity of ammonia gas released from urea decreases. If we look at the time-dependent diagram (Figure 4), the reaction yield decreases after 3 hours. This is because the amine groups in the formed terephthalamide begin to decompose. Figure 5 shows the effect of inorganic salts used as catalysts on the reaction yield. This diagram shows that a catalyst can significantly increase the reaction yield. When NaCl was used as a catalyst, the reaction yield was higher than other catalysts. (Scheme 2). In the reaction, the amine salt of terephthalic acid is initially formed as an intermediate product and decomposes during the reaction to form terephthalamide.

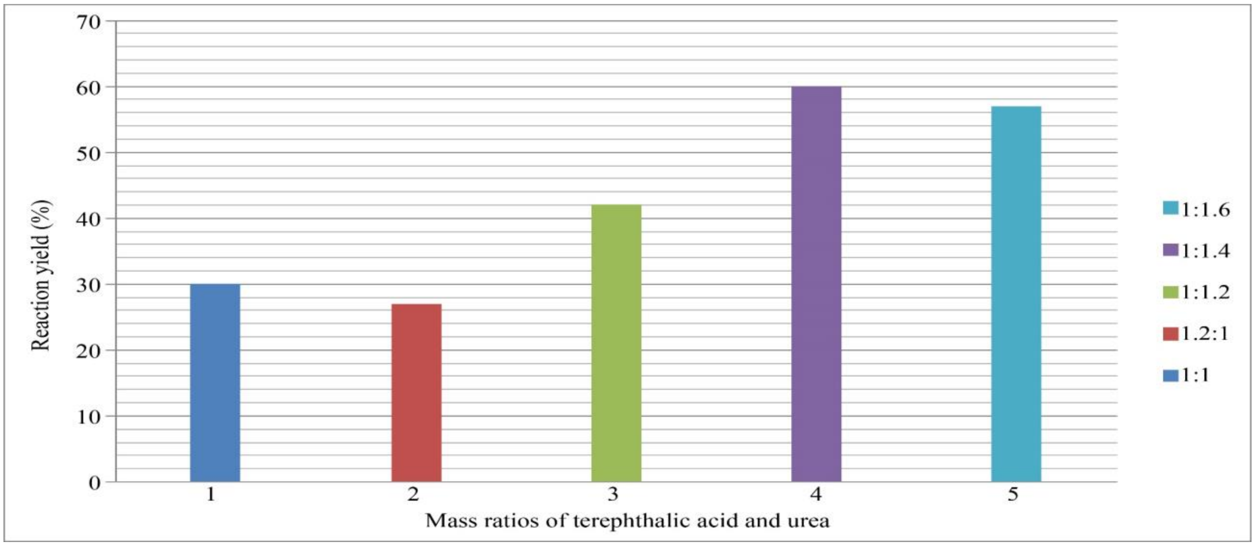


Fig. 1 Relationship between the reaction yield of different mass ratios of terephthalic acid and urea

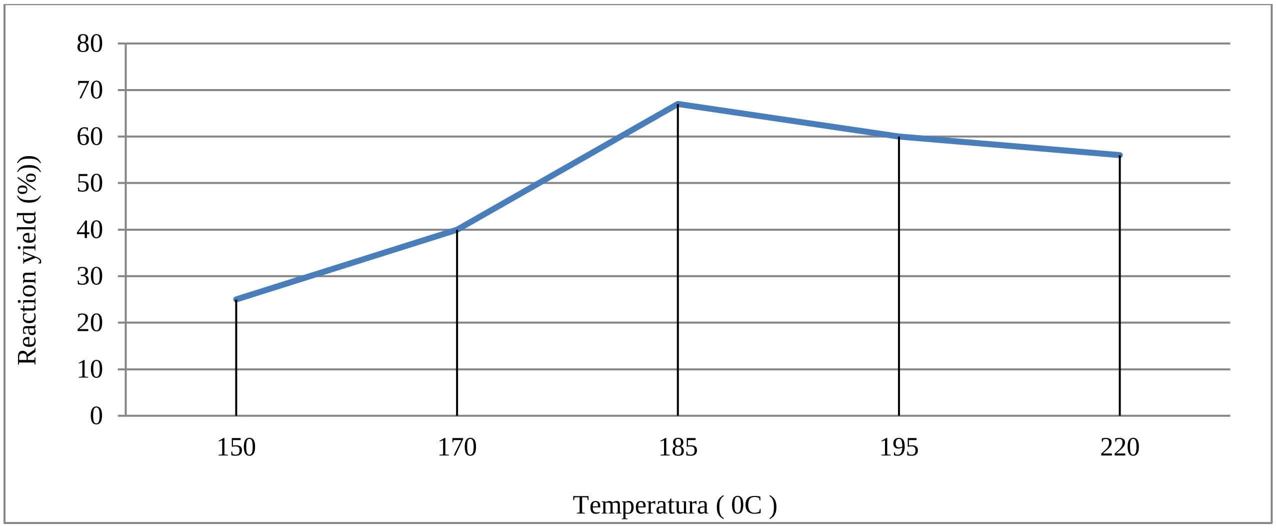


Fig. 2 Temperature dependence of reaction yield

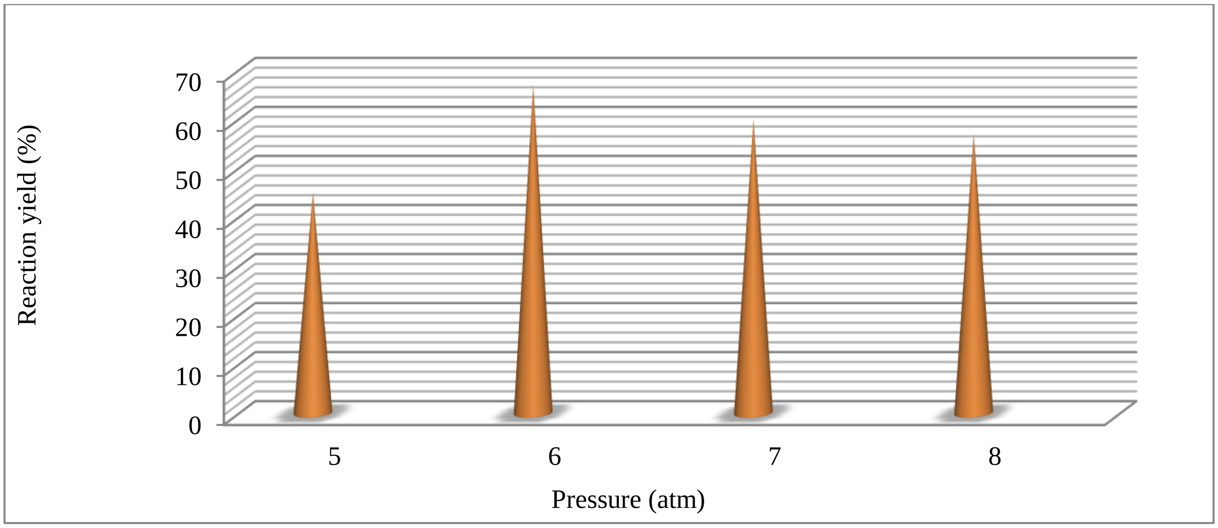


Fig. 3 Pressure dependence of reaction yield

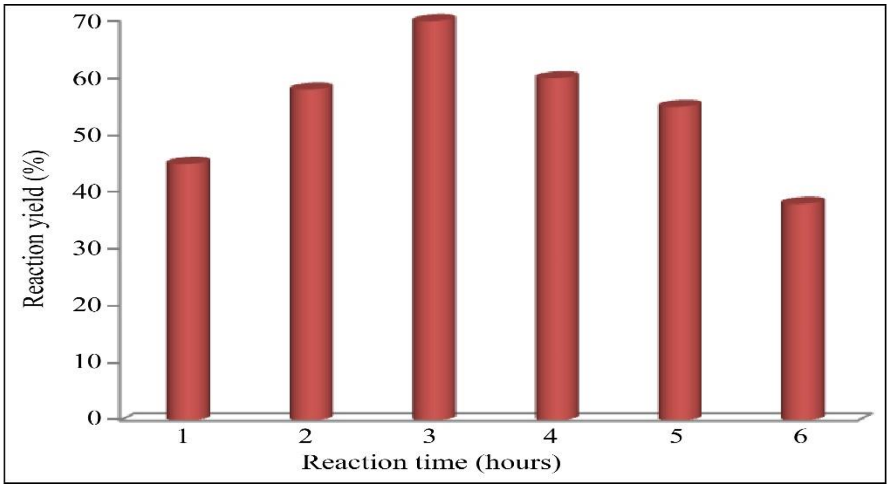


Fig. 4 Time dependence of reaction yield

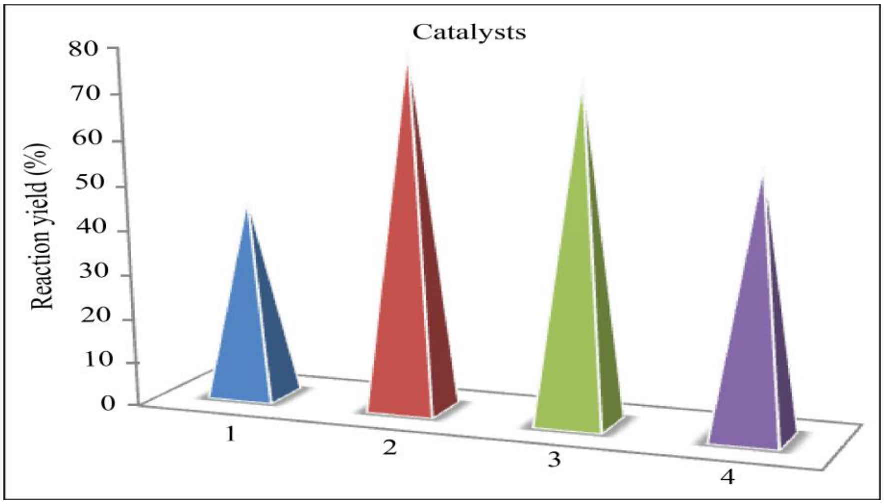
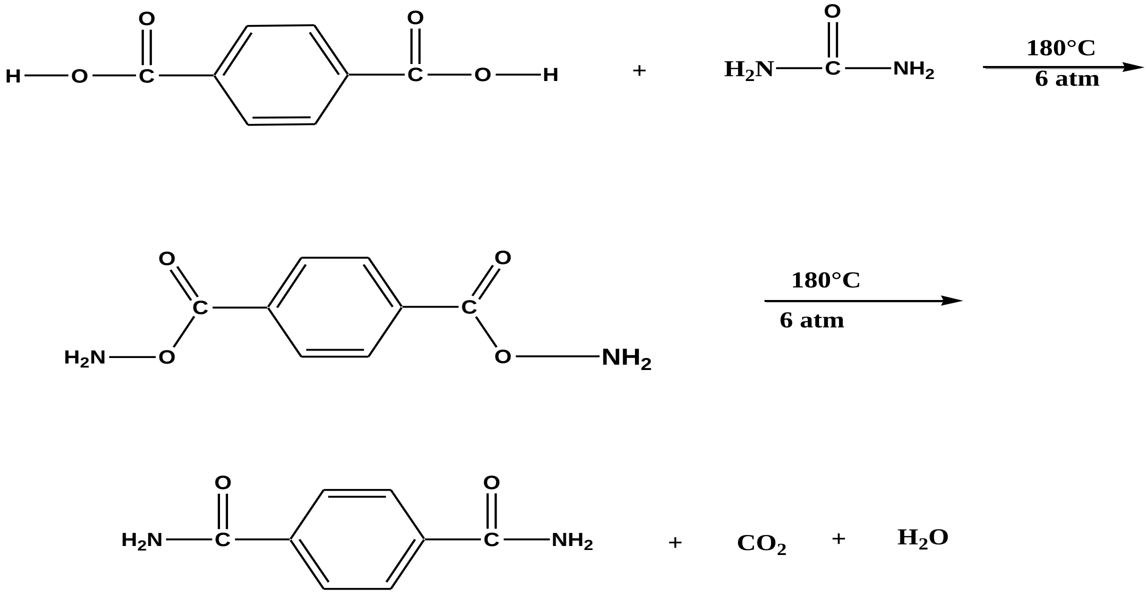


Fig. 5 Effect of catalyst on reaction yield 1. CuCl2 2. NaCl 3.Ca(OH)2 3.MgSO4



Scheme 2. Terephthalamide synthesis reaction

3. Methods

3.1. Infrared Spectrum (IR) Analysis

The structure of the obtained substances was determined using IR spectroscopy (IR-Fure spectrometer manufactured in Japan). IR spectroscopic analyses were performed using the powder method on a SHIMADZU infrared spectrometer (range 4000-600 cm-1, resolution 4 cm-1).

3.2. Raman Analysis

UV Raman spectrometer determines a substance molecule's various bonds and structural arrangements. The results obtained through this method can be used to identify various functional groups in a sample.

3.3. Nuclear Magnetic Resonance Spectroscopy (NMR) Analysis

A radio spectroscopy device that examines the interaction between matter and radiofrequency radiation. It is predicated on the phenomenon of magnetic resonance and resonant transitions among the magnetic energy levels of atomic nuclei within an external magnetic field. It is utilized to examine molecule structure, intermolecular interactions, and dynamics.

3.4. Thermogravimetric (TGA) and Differential Thermal (DTA) Analysis

SHIMADZU (Simultaneous Thermal Analysis) is a versatile, reliable, high-performance thermal analysis platform designed for simultaneous TGA-DTA and TGA-DSC analysis methodologies. It is used for various research purposes, including component identification and measurement of optical properties of samples.

4. Results and Discussion

4.1. IR Spectrum of the Analysis

Figure 6 shows the IR spectrum of terephthalic acids obtained by the alkaline method. In this, we can see different peaks, and by analyzing them, we can observe the stretching vibration frequencies of the C=O carbonyl group in the region of -1678.07 cm^{-1}. In the spectral region of 1510.26 cm^{-1}, indications are arising from the stretching vibrations of the C=C bonds of the aromatic ring. In the region of 1423.47 cm^{-1}, we can see the CH group and the stretching vibrations of the C-O functional group at 1169.4 cm^{-1} and 1123.9 cm^{-1}.

We also used the results of IR spectrum analysis to determine the yield of terephthalamide, its reaction yield, and the most effective starting material ratio. We also used it to determine the best quality, purity, temperature, and pressure.

In Figure 7, the analysis of the spectrum of terephthalamide shows that the asymmetric and symmetric stretching vibrations of the NH_2 groups are in a doublet state in the regions of 3353.21 cm^{-1} and 3155.54 cm^{-1}. The deformation vibrations in the same group are observed in 1653.2 cm-1 and 1614.42 cm-1 regions. 1408.04 cm^{-1} 1373.32 cm^{-1} indicate the CH functional group in the aromatic ring.

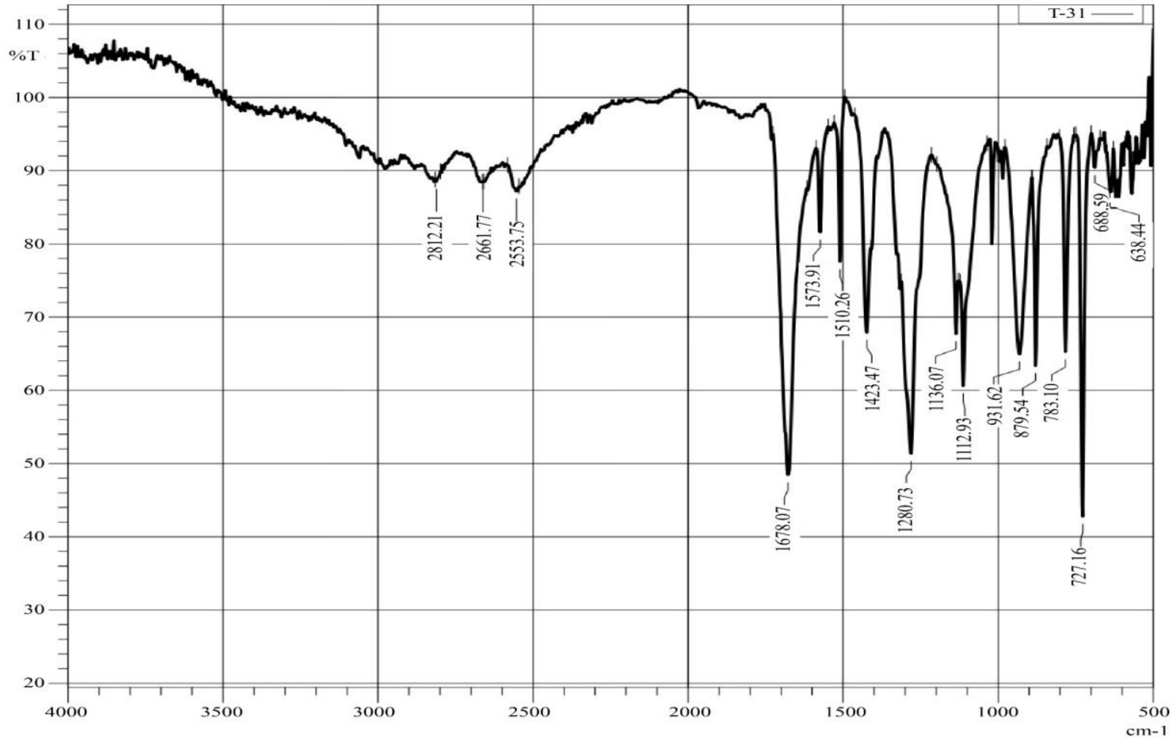


Fig. 6 Terephthalic acid IR spectrum

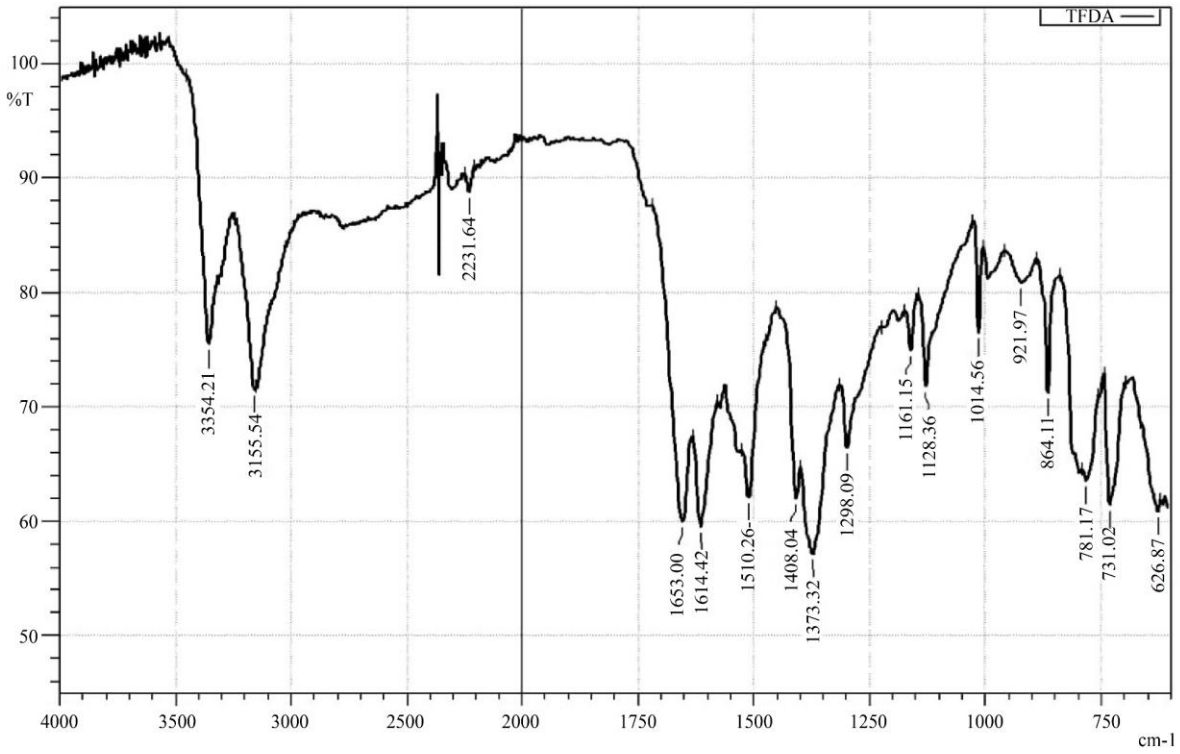


Fig. 7 IR spectrum of the resulting terephthalamide

4.2. Raman Analysis Spectrum

When analyzing a sample of terephthalamide in the Raman spectrum, the deformations of the benzene ring can be seen in the regions of 327.46 cm^{-1}, 457.08 cm^{-1} and 683.64 cm^{-1}, the C-N bond at 1285 cm^{-1}2, the C-N bond at 1616–1687 cm^{-1} in =O and C=C and the C-H bonds in the aromatic ring at 3062 cm^{-1} (Figure 8).

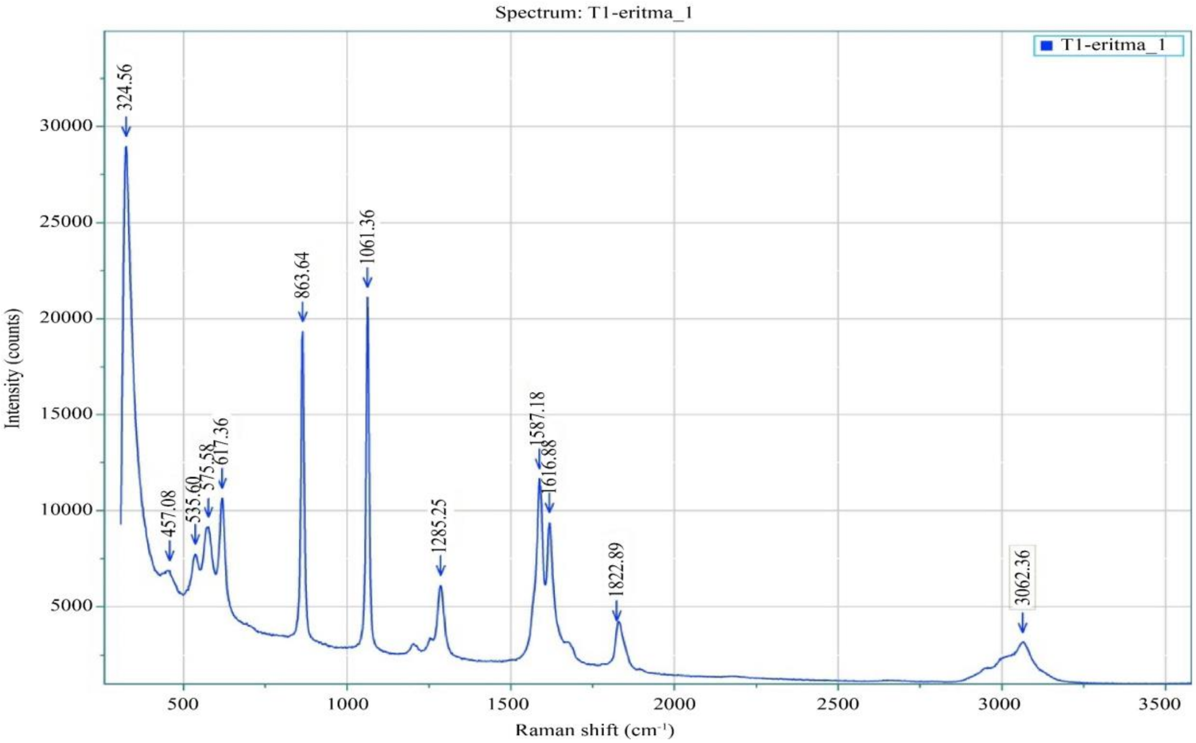


Fig. 8 Raman spectrum of the resulting terephthalamide

4.3 . Differential Thermal and Thermogravimetric Analysis

In the DTA analysis of the obtained terephthalamide, only one endothermic peak was observed at 324.93 oC. This was associated with the cleavage of covalent bonds between simple atoms. The amount of energy absorbed for this process was -825.34 µcal (- 644.56 j/g) (Figure 9).No exothermic state was observed in the process. In thermogravimetric analysis, mass loss occurred in 3 stages. In stage 1, the total mass decreased by 2.65% between 26.33 °C and 226.88 °C. In stage 2, 73.7% of the total mass was decomposed between 226.88 °C and 417.57 °C, the largest mass loss. In the final stage, 8.6% of the total mass was lost between 417.57 °C and 601.74 °C.

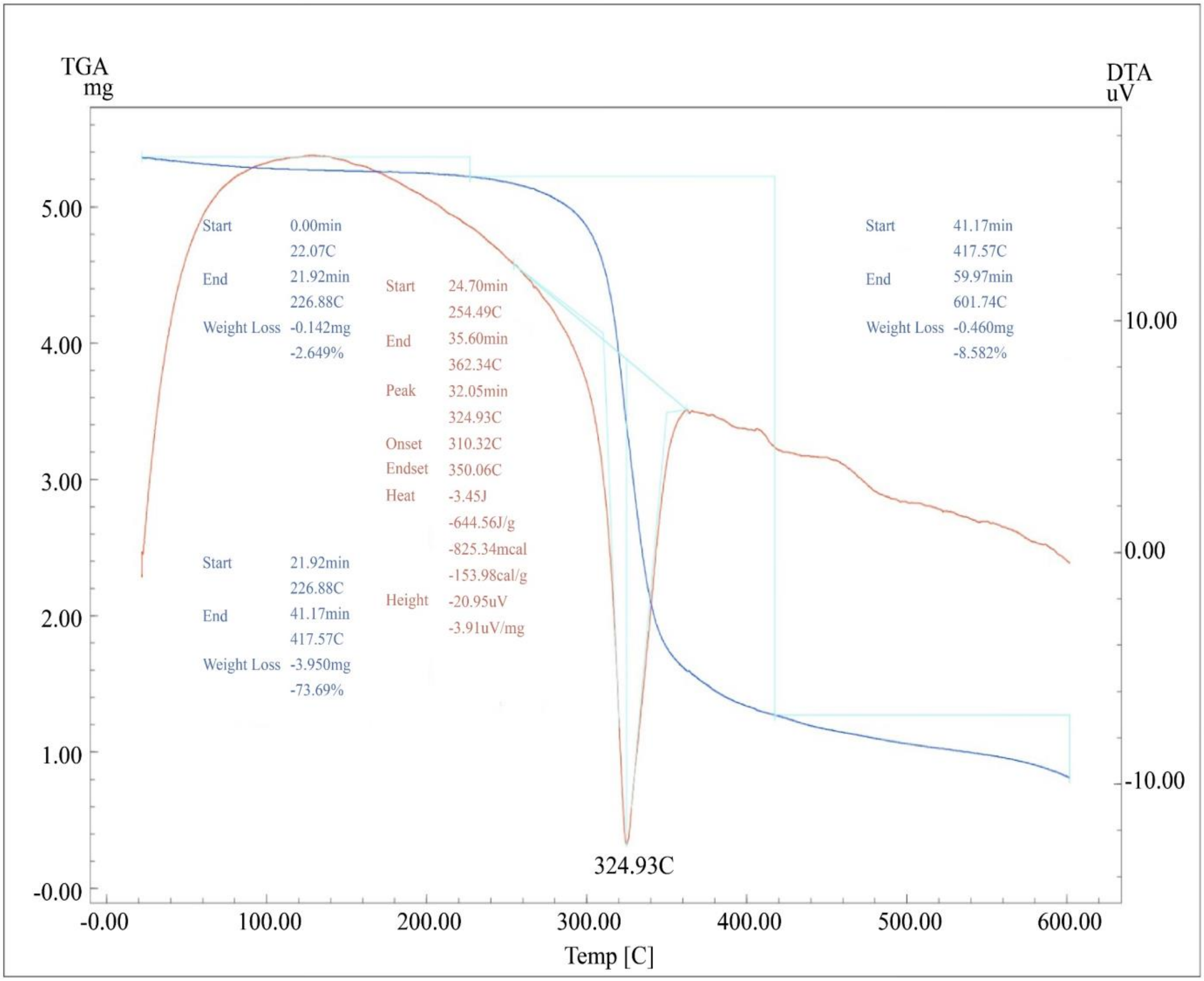


Fig. 9 Derivatogram and thermogravimetric analysis of the resulting terephthalamide sample

Table 1. TGA analysis of the obtained terephthalamide

Reaction Process	Reaction Process Duration (min)	Temperature Range (˚C)	Mass Loss (%)
1-bosqich	21.92	26,33ºC-226,88ºC	2,65 %
2-bosqich	19.25	226,88ºC -417,57ºC	73,7%
3-bosqich	18.8	417,57ºC - 601,74ºC	8,6%

4.4. NMR Analysis

The 1H NMR for terephthalamide is shown in Figure 9. The protons at δ 7.92 ppm correspond to the aromatic ring. NH2 protons probably contribute to the signals at δ 6.55 and 8.5525 ppm (Figure 10). The 13C NMR spectra of terephthalamide are shown in Figure 10, with peaks at δ 128.93 ppm and 127.7 ppm corresponding to aromatic carbons. The peak at δ 167.03 ppm corresponds to the amide carbonyl carbon, characteristic of the CONH2 group in terephthalamide (Figure 11).

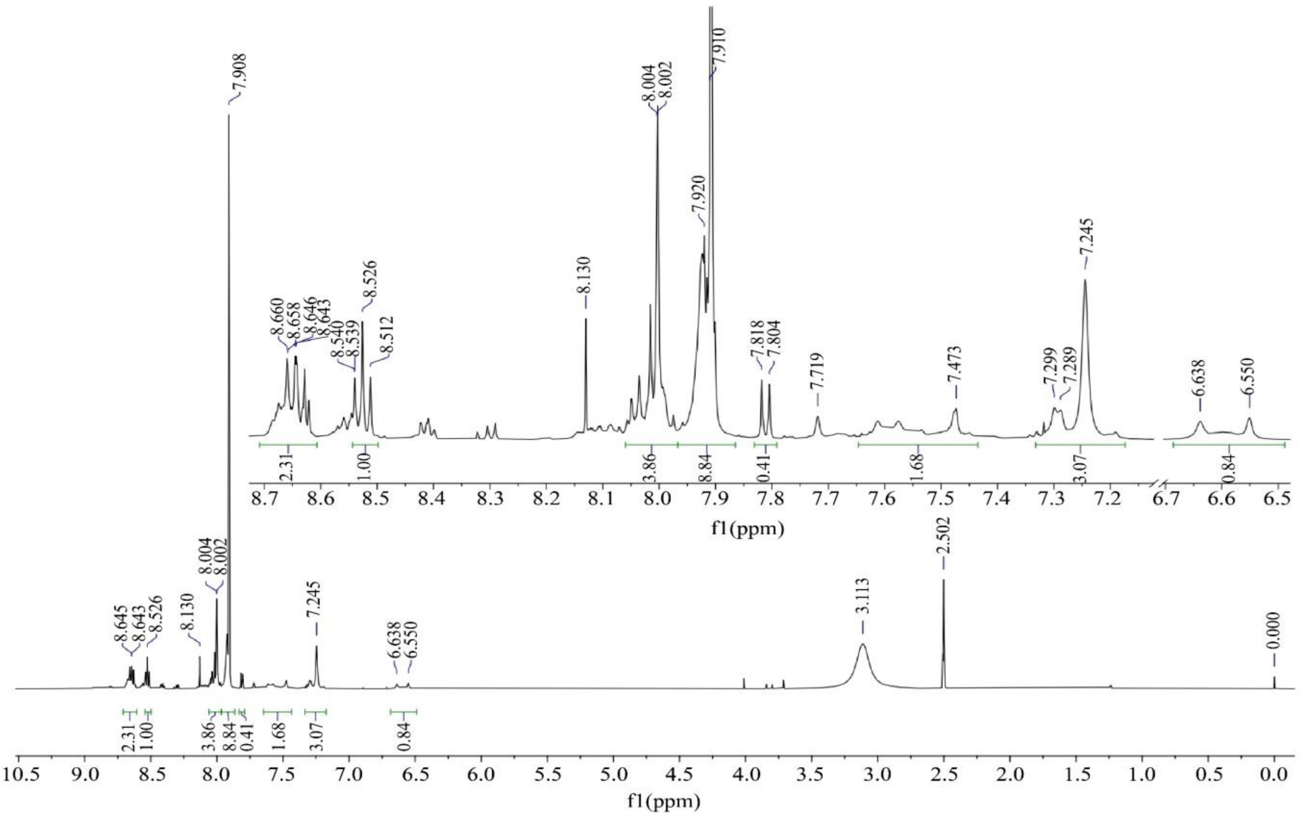


Fig. 10 The result of NMR analysis of the obtained terephthalamide

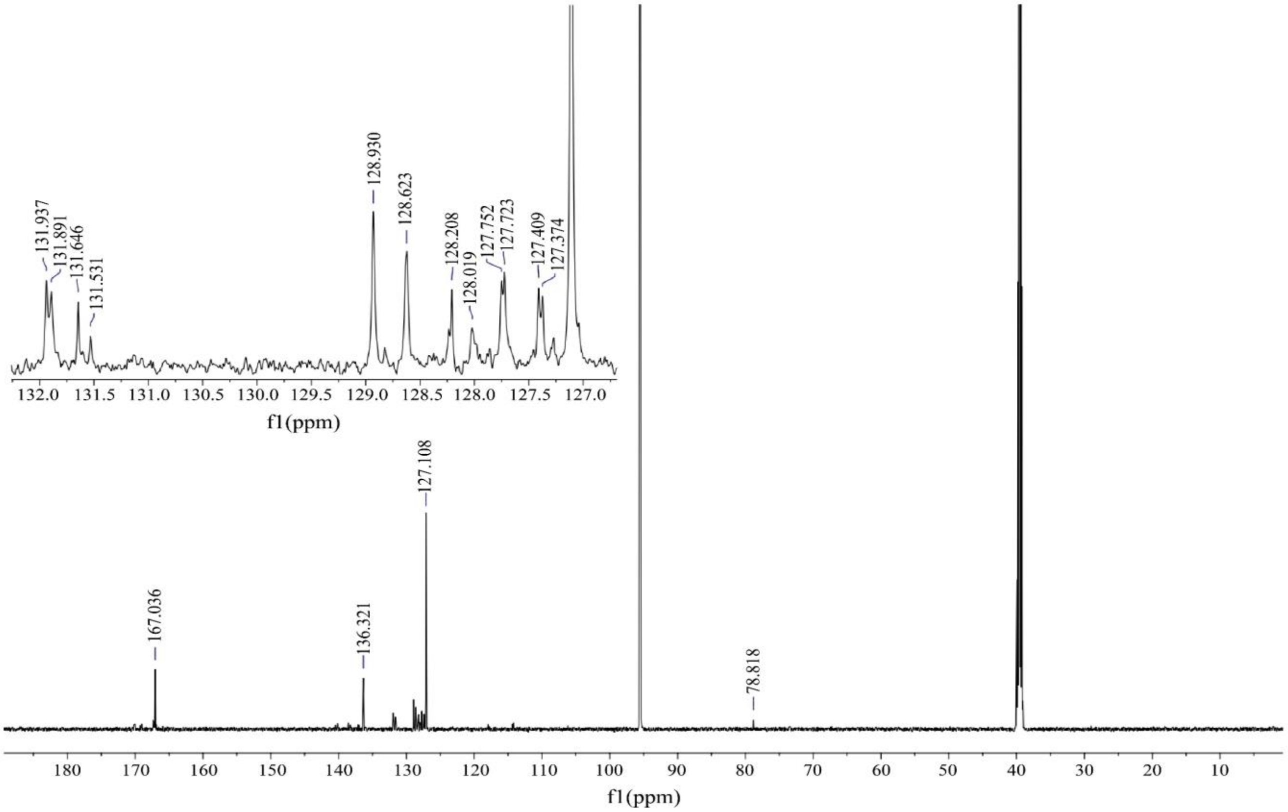


Fig. 11 PMR analysis result of the obtained terephthalamide

5. Conclusion

As a result of our research, terephthalamide was synthesized from secondary waste, and the factors affecting it (pressure, temperature, mass ratios of starting materials) were studied.

The reaction yield was also increased. It was found that the reaction yield can be increased by 10-15% by using catalysts during the reaction process.

By comparing the IR and Raman spectra of terephthalamide and the starting materials and analyzing the results of TG and DTA analyses, it was determined that aromatic rings, carbanyl and amine groups were present.

At the same time, the NMR results proved that the obtained product contained functional groups related to terephthalamide.

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Authors' Declaration

- No conflict of interest exists.
- We formally assert that all figures and tables in the manuscript are our own.
- Ethical Clearance: The project received approval from the local ethics council at Termez State University.

Authors' Contribution Statement

Original draft-writing-T. R. Saidnazarov. Saidnazarov T.R.: The organizational and editing of work. Turaev Kh. Kh.: the paper's proofreading and editing. The provision and certification of software by Karimov M. . Qosimov Sh.A. Akhatov A.A: The original manuscript, concept, investigation, and visualization of writing.

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