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DEPOLYMERIZATION OF WASTE PET WITH NAOH USING MICROWAVE REACTOR

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By Khaldoon Tareq Ibrahim AL-BAITAR

October 2023

We certify that we have read this thesis and that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science

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ABSTRACT

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Master of Science in Chemical Engineering

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Environmental pollution is one of the major problems facing current and future urban life, and it also poses a major threat to the world's natural environment. Therefore, one of the most pressing concerns is the need for efficient waste management. One of the most important environmental pollutants is plastic, including polyethylene terephthalate (PET) containers, which constitute a large percentage of plastic. Polyethylene terephthalate is the main material from which plastic bottles are made. It is most common in water bottles, where packaging materials (food and beverages) are common. The main methods used to dispose of plastic waste are burial and incineration. These methods may cause environmental problems, such as the leakage of waste into riverbeds or the generation of gases that are harmful to the environment. Due to the thermo-physical properties of the plastic, it is converted into low-value products, resulting in an economic loss. Therefore, chemical recycling is the ideal alternative for recovering raw materials (PET). The focus of this study was on the chemical depolymerization and production of terephthalic acid (TPA) using alkaline hydrolysis in the presence of titanium dioxide as a catalyst and using a microwave (MW) irradiation reactor for heating and controlling the reaction conditions in terms of temperature and time. For our design experiments, the TAGUCHI DESIGN method and analysis of variance (ANOVA) were used to analyze the product, which is terephthalic acid (TPA), where the temperatures were (165, 180, 195)C, the time was (10, 20, 30) minutes, and the amount of catalyst (0.01, 0.02, 0.03) g, base concentration NaOH% (12, 8, and 4) to conduct PET depolymerization experiments. Statistically, the most influential variable on depolymerization was identified, as the F value for temperature was (92.88),

followed by the base concentration, which reached an F value of (46.95), while time and the amount of the catalyst TiO_2 showed similar proportions, with their (F) values reaching (30.07) and (32.70). Respectively, the (p) value was found for all variables, as it reached zero(0), meaning that the probability of an error occurring is very small. The effect of the factors among them on the remaining PET was demonstrated through graphics, where contour plots were drawn using the Mini Tab program, which showed that temperature is the largest influence on the depolymerization of PET. Through other drawings, the relationship was explained in detail between the variables and the amount of remaining PET, and a linear regression equation was also created to find the effect of each variable separately on the amount of remaining PET. TPA was produced with high productivity, reaching 99.9% during laboratory experiments. The results were examined by FTIR, HNMR, and microscopy. The results showed a high degree of purity in the product resulting from the experiments. Therefore, this study not only presents an innovative solution to the pressing challenge of PET waste but also underscores the critical role of chemical recycling in the pursuit of environmental sustainability. Beyond merely recovering materials, our proposed approach represents a significant stride toward resource conservation, promising to impart substantial economic value to the realm of plastic sustainability. As we navigate the complex landscape of environmental stewardship, this research contributes a comprehensive and forward-thinking perspective to the evolving field of waste management and sustainable material recovery.

2023, 96 pages

Keywords: Alkaline hydrolysis, Depolymerization, Polyethylene terephthalate (PET), Terephthalic acid (TPA), Microwave irradiation (MW), Titanium dioxide (TiO_2)

ÖZET

ATIK PET'İN MİKRODALGA REAKTÖR KULLANILARAK NAOH İLE DEPOLİMERİZASYONU

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Ekim 2023

Çevresel kirlilik, mevcut ve gelecekteki kentsel yaşamın karşılaştığı temel sorunlardan biridir ve aynı zamanda dünya doğal çevresine büyük bir tehdit oluşturur. Bu nedenle, en acil endişelerden biri etkili atık yönetiminin gerekliliğidir. Plastik, en önemli çevresel kirleticilerden biridir ve bunun içinde polietilen tereftalat (PET) konteynerleri, plastik oranının büyük bir bölümünü oluşturan önemli bir faktördür. Plastik şişelerin ana malzemesi olan polietilen tereftalat, genellikle su şişelerinde, yemek ve içecek ambalajlarında yaygın olarak kullanılır. Plastik atıkların bertarafı için kullanılan temel yöntemler gömme ve yakmadır. Bu yöntemler, atıkların nehir yataklarına sızmasına veya çevreye zararlı gazların oluşmasına neden olabilir. Plastiğin termo-fiziksel özellikleri nedeniyle, düşük değerli ürünlere dönüştürülerek ekonomik kayıplara yol açabilir. Bu nedenle, kimyasal geri dönüş, ham madde (PET) geri kazanımı için ideal bir alternatiftir. Bu çalışmanın odak noktası, alkalen hidroliz varlığında titanyum dioksit katalizörü kullanılarak kimyasal depolimerizasyon ve tereftalik asit (TPA) üretimidir. Reaksiyon koşullarını, sıcaklık ve süre açısından kontrol etmek için mikrodalga (MW) ışınları kullanılarak gerçekleştirilen deneylerde TAGUCHI TASARIM yöntemi ve varyans analizi (ANOVA) kullanıldı. Tasarım deneylerimizde, sıcaklıklar (165, 180, 195)°C, süreler (10, 20, 30) dakika ve katalizör miktarı (0.01, 0.02, 0.03) g, baz konsantrasyonu NaOH% (12, 8 ve 4) olarak PET depolimerizasyon deneyleri gerçekleştirildi. İstatistiksel olarak, depolimerizasyon üzerinde en etkili değişken sıcaklık için (92.88) F değeri olarak belirlendi, onu baz konsantrasyonu takip etti ve (46.95) F değerine ulaştı, süre ve TiO_2 katalizör miktarı benzer oranlarda (F)

değerleriyle (30.07) ve (32.70) ulaştı. Sırasıyla, tüm değişkenler için (p) değeri sıfır (0) olarak bulundu, bu da bir hata olasılığının çok düşük olduğu anlamına gelir. Değişkenler arasındaki etkisi PET üzerinde kalan miktar üzerinden grafiklerle gösterildi, Mini Tab programı kullanılarak çizilen kontur grafikleri, sıcaklığın PET depolimerizasyonu üzerindeki en büyük etkiyi gösterdi. Diğer çizimler aracılığıyla, değişkenler arasındaki ilişki ayrıntılı olarak açıklandı ve her değişkenin PET üzerinde kalan miktar üzerindeki etkisini bulmak için bir doğrusal regresyon denklemi oluşturuldu. TPA, laboratuvar deneylerinde %99.9'luk yüksek verimlilikle üretildi. Sonuçlar FTIR, HNMR ve mikroskopi ile incelendi. Sonuçlar, deneylerden elde edilen üründe yüksek derecede saflık gösterdi. Bu nedenle, bu çalışma sadece PET atığıyla ilgili acil bir soruna yenilikçi bir çözüm sunmakla kalmaz, aynı zamanda çevresel sürdürülebilirliğin peşinde kimyasal geri dönüşümün kritik rolünü vurgular. Sadece malzemeleri kurtarmaktan öte, önerdiğimiz yaklaşım, plastik sürdürülebilirliği alanında önemli bir adım olarak kaynak koruma konusunda önemli ekonomik değer vaat ediyor. Çevresel sorumluluğun karmaşık manzarasında gezinirken, bu araştırma atık yönetimi ve sürdürülebilir malzeme geri kazanımının evrimleşen alanına kapsamlı ve ileri görüşlü bir bakış açısı sunar.

2023, 96 sayfa

Anahtar Kelimeler: Alkali hidroliz, Depolimerizasyon, Polietilen tereftalat (PET), Tereftalik asit (TPA), Mikrodalga ışınlama (MW), Titanyum dioksit (TiO_2)

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Khaldoon Tareq Ibrahim AL-BAITAR
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LIST OF SYMBOLS

dL / g	Deciliters per gram
Iv	Intrinsic viscosities
µm	Micro meter
Mt	Million metric
Vol	Volume
Wt	Weight

LIST OF ABBREVIATIONS

ANOVA	Analysis of variance
BHET	Bis(2-hydroxyethylterephthalete)
CAGR	Compound annual growth rate
DES	Deep eutectic solvents
DES 1	Deep eutectic solvents based (choline chloride-urea)
DES 2	Deep eutectic solvents based (choline chloride-thiurea)
DOE	Design of experiments
DEG	Di Ethylene glycol
DMT	Dimethyle Terephthalete
EG	Ethylene glycol
FTIR	Fourier transform infrared
KMH	KOH-in-methanol
LFG	Landfill gas
MW	Microwave irradiation
PTC	Phase transfer catalyst
PC	Polycarbonates
PET	Polyethylene terephthalate
HNMR	Proton nuclear magnetic resonance
NaOH	Sodium hydroxide
DMSO	Sodium methoxide in methanol and dimethyl
TPA	Terephthalic Acid
THF	Tetrahydroflurane
TiO_2	Titanium dioxide
WTE	Waste to energy

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1. INTRODUCTION

1.1 Plastics

The words "plastic" and "plasticus," both of which mean "formable or moldable in a cast," are derived from Greek and Latin. It and the word resin are frequently used interchangeably (Kim and Lee 2020). The first "completely synthetic plastic" to enter the market was bakelite. it bears the name of its creator, born-Belgian scientist Leo Baekeland developed in the early in (1900s), The reaction of formaldehyde, produced from the mixture of coal and water, and phenol, derived from coal tar, led to the creation of Bakelite (Barot *et al.* 2019).

Plastic is a resource that has changed people's lives since it was first manufactured. It contains numerous synthetic or semi-synthetic chemical molecules with high molecular weight (Lear *et al.* 2021) Synthetic organic polymers used to make plastics are typically derived from petrochemical feedstocks (Cywar *et al.* 2022) Also Plastic is produced by polymerizing or polycondensing natural materials such as cellulose, coal, natural gas, salt, crude oil, minerals, and plants into mass and other malleable substances that may be molded into solid objects. It is a versatile material with a wide range of applications(Saifuddin Syed Salahuddin and Suganchand Zambani, 2020)Due to the distinctive qualities of plastics, which include their light weight, low cost, robustness, durability, strength, resistance to corrosion, thermal and electrical insulation, and versatile fabrication and design capabilities that allow for the easy molding of a variety of products, plastic finds use in a wide variety of applications (Thompson *et al.* 2009).

Global production for (resins and fibers)only increased from 2 million metric (Mt) in 1950 to 380 Mt in 2015, a compound annual growth rate (CAGR) of 8.4% (Geyer 2020) At various levels of effort to estimate plastic waste to 2030 for 173 countries, 19 to 23 Mt of plastic waste produced globally in 2016 ended up in aquatic habitats (sea or river). Given the stringent targets currently set by countries, annual emissions could

reach 53 Mt annually by 2030 (Borrelle *et al.* 2020). Unfortunately, an increase in the application and use of plastic has driven an increase in the generation of plastic waste. The majority of this waste has been disposed of in landfill. If current practices continue, it is estimated that by 2050, there will be 12,000 Mt of plastic waste in landfills or in the natural environment. Not only does this volume of waste represent a huge loss of valuable materials, but it also poses a huge risk to the environment and wildlife, as plastic takes hundreds of years to decompose, it can be accidentally ingested by animals, and it can get involved with wildlife to either injure or kill them (Davidson *et al.* 2021)

1.2 Classification of Plastic

Based on their characteristics when heat is applied, plastic materials are divided into thermosetting and thermoplastic (Evode *et al.* 2021). Plastics also can alternatively be divided into two categories: (i) crystalline or semicrystalline plastics, such as polyamides, polyesters, polyethylene, polypropylene, polyvinyl chloride, and some polyurethanes; and (ii) amorphous plastics, such as polystyrene and polymethyl methacrylate (Nanda and Berruti 2021). Plastics can also be divided into biodegradable and non-biodegradable categories based on their capacity to degrade. Bioplastics created from plant waste and biopolymers are biodegradable in contrast to traditional plastics, which are made of petrochemicals (Ahmed *et al.* 2018).

1.2.1 Thermosetting plastics

In this type, when the plastic is heated,it goes through chemical processes, followed by a single melting and forming step before solidification. An irreversible chemical reaction occurs during the thermosetting process. Polyethylene, polypropylene, polystyrene, and polyvinyl chloride are examples of thermosetting plastics. (Nanda and Berruti 2021) All the tiny molecules are chemically joined to create a single, massive network molecule during curing. The structure of thermosetting plastics resembles a chain and is similar to thermoplastics before molding. The process of curing involves the crossing of neighboring molecules, creating a complicated web of connections. They

are distinguished from linear polymers (thermoplastics) by being called the addition of heat, This cross-bond prevents the slippage of individual chains, inhibiting plastic flow with the addition of heat (Figure 1.1) (Mukrimaa *et al.* 2016).

1.2.2 Thermoplastics

Regardless of how frequently the procedure is repeated, thermoplastics soften when exposed to heat and harden when they are cooled. They may be repeatedly molded by heating and chilling in alternation They are liquids that resemble rubber when they are melted, and they are glassy or partially crystalline when they are solid (Mukrimaa *et al.* 2016). Thermoplastics are pliable because their linear molecular structure remains unchanged when heated and because they dissolve in solvents with a similar polarity. Thermosets undergo dramatic changes in their characteristics after primary covalent crosslinking, becoming insoluble and infusible while increasing in modulus, creep resistance, maximum use temperature, and chemical resistance while decreasing in extensibility (Sobkowicz-kline *et al.* 2017).

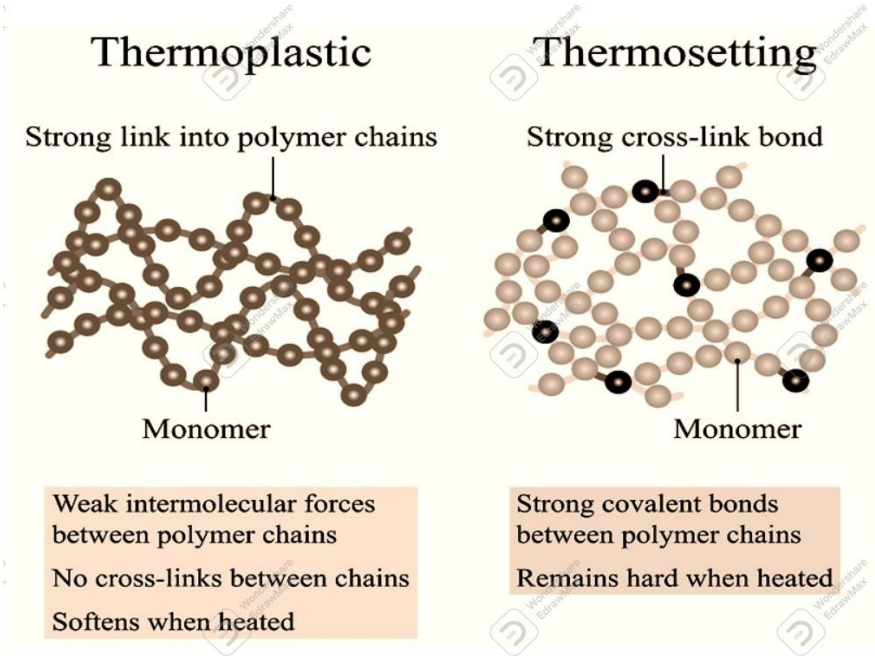


Figure 1.1 Thermoseting and thermoplast structure (Kazemi *et al.* 2021)

1.3 Polymers

A polymer is a large molecule constructed from many smaller structural units called monomers, covalently bonded together in any conceivable pattern. In certain cases, it is more accurate to call the structural or repeat unit a monomer residue because atoms are eliminated from the simple monomeric unit during some polymerization processes (Evode *et al.* 2021). These monomers serve as the foundation for polymers. Different monomer mixtures result in plastic with various properties, such as strength or shaping ability (Rosenboom *et al.* 2022).

1.3.1 Polymerization

The process of creating macromolecules, known as polymerization, involves joining together monomer molecules through chemical processes. Polyethylene, a typical sample that may comprise molecules with 50,000 carbon atoms linked together in a chain, is produced by the polymerization of ethylene, for instance. This long-chain nature of polymers distinguishes them from other materials and gives birth to their distinctive feature (Young and Lovell 2011).

The plastics industry relies heavily on polyethylene. It is a polymer of ethylene that is made at high temperatures and pressures to achieve the desired qualities. Its structural formula is (CH_2=CH_2),and its empirical formula is (-CH_2-CH_2-)n. Polyethylene can withstand contact with many different chemicals without suffering any damage (Evode *et al.* 2021) We can classify polymers into four main entails and sub entails shown in (Figure 1.2) (Vendan *et al.* 2018).

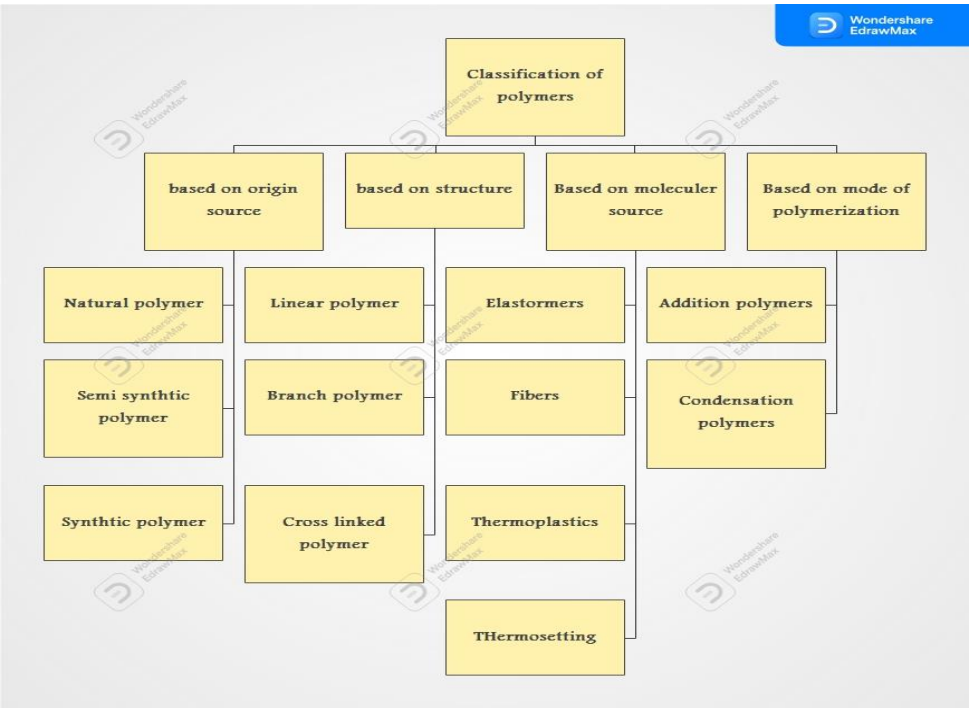


Figure 1.2 Classification of polymers (Vendan *et al.* 2018)

1.4 Recycling Plastic

Polymers and additives make up plastics. The proportion of polymers that a plastic material contains can range widely, depending on it, from almost 100% to less than 20% of the material (Okan *et al.* 2019), the most popular polymers, including low- and high-density polyethylene, polypropylene, polystyrene, polyvinyl chloride, and polyethylene terephthalate, were created and put through various processes (Rodrigues *et al.* 2018). In the past, recycling in the plastics sector took place within firms that produce goods as a standardized process For instance, in extrusion, materials and If contamination restrictions permitted, internal scrap would be reprocessed with virgin material to increase the yields of the final product (Mulvaney *et al.* 2021), Regarding the issues with plastic recycling. This was motivated by two elements: a rising worry about the costs and both monetary and ecological effects of landfilling, and the overwhelming amount of plastic entering that trash stream with waste (Santos *et al.* 2023). Landfill emerges as the most common method of plastic waste disposal, followed by incineration with waste-to-energy (WTE). chemical recycling methods manage the lowest volume of plastic waste (Tsui and Wong 2019).

Managed landfills may have some benefits. A landfill without a leak can act as a "carbon sink" for plastic waste. Landfills produce harmful gases that can harm both marine and terrestrial life. Most waste gas systems (landfill gas [LFG]) use methane and carbon dioxide (up to 90%), which are produced when methanogenic substances such as CO, N_2, alcohol, hydraulic carbon, organic acid compounds, and heavy metals decompose (Rajmohan *et al.* 2019, Blair and Mataraarachchi 2021).

1.4.1 Plastic waste recycling options

Mechanical recycling: Plastic trash is mechanically recycled into secondary raw materials or products without appreciably altering the chemical structure of the substance (Santos *et al.* 2023). The use of separation techniques, crushing, heat, and extrusion to melt used plastic waste down and produce recycled plastic pellets.

The conversion of trash to fresh raw materials must occur before the actual reprocessing of recycled materials into new goods. This phase, known as the 'End-of-Waste' phase, follows the collecting stage. The following steps may be included in this process:

1. Sorting and separation: take place depending on the shape, density, size, color, or chemical makeup.
2. Baling: If the plastic is not treated where it is sorted, it is frequently baled in between for shipping.
3. Washing: the removal of impurities (typically organic).
4. Grinding is the process of reducing the size of items to flakes.
5. Compounding and pelletizing: optional reprocessing of flakes to create granulate, which is easier to employ in converters than flakes (Ragaert *et al.* 2017).

Chemical/feedstock recycling: The use of thermal and/or chemical techniques to break down plastic waste into its consistent parts, such as monomers, oligomers, or liquid, solid, and gaseous hydrocarbon mixes (Davidson *et al.* 2021).

Plastic trash appears to be a very promising feedstock for the manufacture of important chemicals and fuels. The current focus is not only on energy conservation or mechanical recycling, but also on the creation of useful goods like monomers and petrochemical feedstocks. Chemical recycling solutions exist for some feedstocks, such as PET and nylon. Because they are closely related to conventional petroleum fractions and have a high hydrocarbon content, there has been a steady increase in interest in using them as feedstock. Plastic garbage contains no substantial amounts of oxygen. As a result, improved carbon efficiency and, thus, larger gross margins can be envisaged (Al-Salem *et al.* 2010).

Chemical recycling is a recognized recycling technology that adheres to "sustainable development" concepts. Because chemically regenerated plastics can be used in many applications, there has been a steady growth in interest in them. Chemical recycling processes are paving the way for trash to be used as a precursor in the production of pure value-added goods for a variety of industrial and commercial purposes. Yet, because of the raw material cost, capital investment, and scale of operation, chemically regenerated polymers are more expensive than virgin material. For example, it has been determined that a PET chemosis must have a minimum throughput of $1.5*10^4$ metric tons per year to be economically viable (George and Kurian 2014).

Pyrolysis:The use of heat in an oxygen-deficient atmosphere to break down the hydrocarbon bonds in plastic waste to produce a range of solid, liquid, and gaseous hydrocarbon products (Davidson *et al.* 2021).

Pyrolysis is an interesting method for feeding hard-to-depolymerize plastic wastes that are currently incinerated and/or disposed of in landfills, such as multilayer packaging, fiber-reinforced composites, polyurethane construction, and demolition debris. These modern multilayer films, in particular, appear to be more difficult to recycle than the simpler metal, paper, and glass packaging they replace (Vermeulen *et al.* 2011)

Gasification : The use of heat and controlled steam, oxygen, and/or air content to break down plastic waste to produce a syngas, hydrogen, and carbon monoxide-rich gaseous

mixture (Heidenreich and Foscolo 2015). The method necessitates the use of an oxidation agent, which is typically a mixture of steam and pure oxygen or just air (Trippe *et al.* 2011). When compared to incineration and other technologies, gasifying plastic waste has many positive environmental effects. Heavy metals (Hg or Cd), dioxins, furans, HCl, SO2, NOx, HF, and others can be discharged into the environment during the incineration process.separation, both of which have a negative influence on overall costs (Salaudeen *et al.* 2018). Gasifiers are commonly used to increase thermal efficiency in power generation. Besides increased thermal efficiency, it also minimizes dangerous product emissions into the atmosphere. Besides the aforementioned gases, the produced syngas contains contaminants such as NH3, H2S, NOx, alkali metals, and tars (Dudyński *et al.* 2015).

Hydrocracking :The use of heat and pressure in an inert, hydrogen-rich atmosphere to break the carbon-to-carbon bonds in plastic waste and add hydrogen to produce solid-liquid, and gaseous hydrocarbons (Davidson *et al.* 2021). The main difference with catalytic cracking of plastics is the addition of hydrogen. The process takes place at elevated hydrogen pressures, roughly 70 atm, and temperatures in the range of 375– 400 ^{o}C. This happens via low-temperature pyrolysis. The presence of hydrogen improves significantly the product quality, i.e. a higher H/C ratio and lower aromatic content. Experiments for different types of catalysts revealed a high yield of paraffin Another main advantage to upgrading the liquid yield of plastic pyrolysis is that heteroatoms are handled excellently and no toxic products such as dioxins are produced through the process (Ragaert *et al*. 2017).

Incineration: The process of burning plastic waste to derive heat. This heat is captured and either used directly to heat buildings or used indirectly to produce electricity. Sometimes called Waste to Energy (WTE) (Makarichi *et al*. 2018). Land restrictions, contamination, and legislation exist all around the world. The disposal of millions of tons of trash is quickly becoming the most pressing issue for environmental management. Instead, improvements in landfill bioreactors, composting, and thermal processes are envisaged in solid waste disposal. Among these, incineration is widely accepted due to its tiny land footprint, massive bulk and volume reduction, and the

ability to recover energy in the form of heat and power (Kanhar *et al.* 2020). Depolymerization : The use of polymer chemistry to reverse polymerization reactions to yield the component monomers and oligomers of plastic, which can then be used in further polymerization reacti (Davidson *et al.* 2021). Depolymerization is the process of breaking down plastics into their constituent monomers or other forms that can be reused or recycled. Several techniques have been developed for depolymerizing plastics, including thermal, chemical, and biological methods (Crippa and Morico 2019). Depolymerization of PET can be accomplished through Hydrolysis, Ammonolysis, Methanolysis, or Glycolysis, resulting in a variety of degradation products (Ghasemi *et al.* 2021).

1.5 Polyethylene Terephthalate (PET)

One of the most important modern plastics to be created is polyethylene terephthalate (PET)a semi-crystalline polymer. The mechanical characteristics of PET, are influenced by its crystallinity level (Salazar-Beltrán *et al.* 2018). virgin PET is a superior material that has Excellent properties of this material include good tensile strength, acceptable thermal stability, chemical resistance, processing potential, colorability, and clarity (Awaja and Pavel 2005). It can be created under standard temperature and pressure conditions. PET can be produced using petroleum hydrocarbons, ethylene glycol, terephthalic acid, and other processes as in Figure (1.3) (Farzi *et al*. 2019).

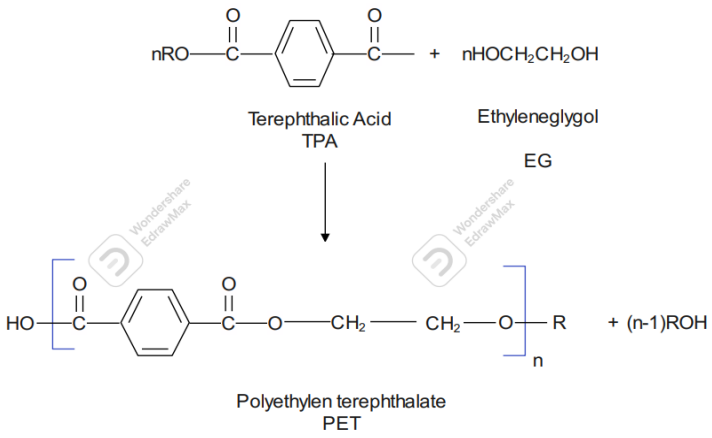


Figure 1.3 PET from EG and TPA reaction (Farzi *et al.* 2019)

This substance is currently widely used throughout the world and is regarded as a thermoplastic polyester material (Padhan *et al.* 2013). Since the 1980s, PET has been used in the beverage sector to create drink bottles. In 1987, more than 700 million pounds of this substance were consumed (Shukla and Harad 2006). PET is utilized as a packaging and container material because of its advantageous physical and chemical characteristics (i.e., carbonated drinks bottles, jars, pipes, sporting goods, etc (Li *et al.* 2016). The intermediates, pure terephthalic acid (TPA) and ethylene glycol (EG), used in the production of PET, are produced from crude oil (Farzi *et al.* 2019). The first result of heating the two components is a mixture of low molecular weight polymers and the monomer bis(2-hydroxyethyl) terephthalate (BHET) (oligomers) (Alzuhairi *et al.* 2017). The mixture then continues to react, separating extra ethylene glycol to generate the PET. The PET is a viscous molten liquid at this point. To create an amorphous substance that resembles glass, it is extruded and water-cooled (Imran *et al.* 2010), some PET is produced utilizing technology based on terephthalic acid's dimethyl ester Closed-Loop Recycling of Polymers Using Solvents (Sherwood 2019).

This successfully eliminates all volatile contaminants such as acetaldehyde, unbound glycols, and water. High molecular weight materials have stiffness, toughness, and creep resistance, as well as enough flexibility to withstand bursting and breaking under pressure. These qualities are essential for good mechanical properties (Sinha *et al.* 2010). The purity of the beginning components is crucial because it is exceedingly challenging to purify a polymer once it has been created. Ethylene glycol can be easily purified using vacuum distillation techniques, whereas terephthalic acid must go through several crystallization procedures. Such high molecular weight and purity materials applications involving food packaging are required (Al-Sabagh *et al.* 2016). Catalysts are used to speed up processes and guarantee viable economics at incredibly low concentrations. Antimony trioxide is the most frequent catalyst, but salts of titanium, germanium, cobalt, manganese, magnesium, and zinc are also used. See figure (1.4) (Mandal and Dey 2019), are also employed, with minor quantities remaining contained inside the polymer chain or the matrix of the polymer. However, other processes, including the reaction of terephthaloyl chloride with ethylene glycol, can be used in the lab to create PET. Although terephthaloyl chloride is more expensive and

toxic than terephthalic acid, this reaction is simpler (Al-Sabagh *et al.* 2016). Polyethylene terephthalate's importance Since the mid-1940s, PET has historically been used to create textile fibers. Nathaniel Wyeth filed for a patent on the PET bottle in 1973, and it became widely used in the 1980s for the manufacture of single-use soft drink bottles (Porta 2019). Polyethylene terephthalate made up the majority of the world's total production of polyesters, which was 25 to 30 million tons in 2000 and rose to 55 million tons in 2012. (PET). The amount of polyester consumed has significantly increased due to the high demand for textile applications, as well as in the food packaging and bottle industries for glass replacement, fibers, and molding resins (Barot *et al.* 2019). The worldwide PET market is now dominated by two PET grades: bottle-grade PET and fiber-grade PET. The primary differences between these standard classes are their molecular weights or intrinsic viscosities (IV), respectively, optical appearance, and production methods. The latter is distinguished by the quantity and kind of co-monomers, stabilizers, metal catalysts, and colorants. grade of textile fiber PET has an intrinsic viscosity between 0.55 and 0.67 deciliters per gram (dL/g) and a molecular weight between 15,000 and 20,000 g/mol (Paszkiewicz *et al.* 2012). The inherent viscosity of the common bottle grade is 0.80 dL/g. Additional PET grades are produced for packaging films and video production and audio cassettes These PET kinds frequently have intrinsic viscosities of 0.64 dL/g and are standard grades. Solid additives with defined particle sizes and particle-size distributions, such as SiO_2 or clay, are added to products to lessen their tendency to stick (Barot *et al.* 2019).

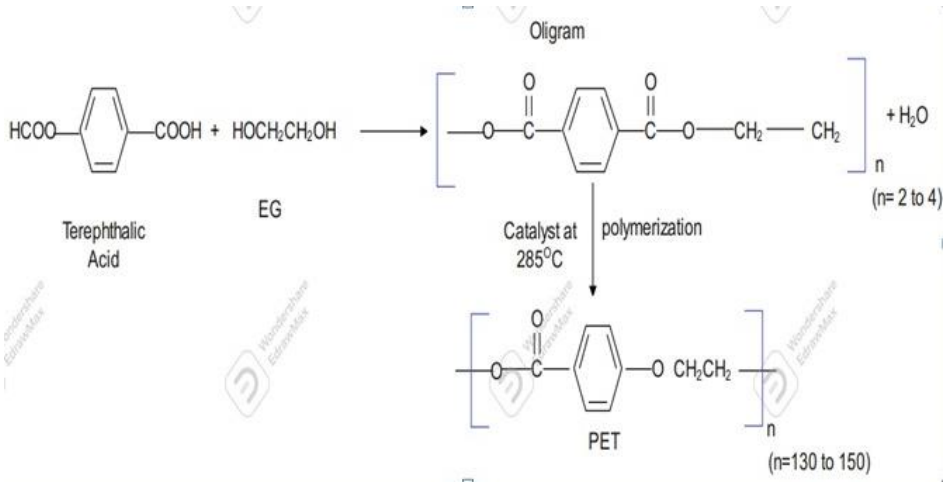


Figure 1.4 Description of the synthesis of PET (Mandal and Dey 2019)

1.5.1 Typical PET properties

Excellent mechanical, electrical, and thermal qualities are included in PET, a form of thermoplastic engineering polyester. In addition, it has excellent transparency, dimensional stability, and moisture absorption resistance. The crucial characteristics are stated.

1. Lightweight and transparent
2. The polymer matrix's very low moisture diffusion
3. Outstanding dimensional stability
4. Outstanding electrical capabilities
5. Outstanding chemical protection
6. Resilience to environmental stress cracks
7. Very good thermal aging resistance
8. Extremely little creep across a broad temperature range
9. Outstanding color stability
10. Excellent resistance to wear
11. Minimal flavor absorption
12. A more appealing aesthetic (compared to other polymers)
13. Easy processing and affordable availability
14. High levels of recyclability (Salazar-Beltrán *et al.* 2018).

1.6 Depolymerization of PET

Referred to as the procedure leading to the complete breakdown of PET into its monomers or partial breakdown into oligomers and other chemical compounds (Siddiqui *et al.* 2010). There have been many chemical procedures used. Glycolysis, methanolysis, hydrolysis, aminolysis, and ammonolysis are the top five methods for chemically recovering waste PET However, the majority of these methods require harsh reaction conditions, like extended reaction times, high temperatures and pressures, or even the presence of significant volumes of concentrated acids or bases. See Figure (1.5) (Mohsin *et al.* 2018).

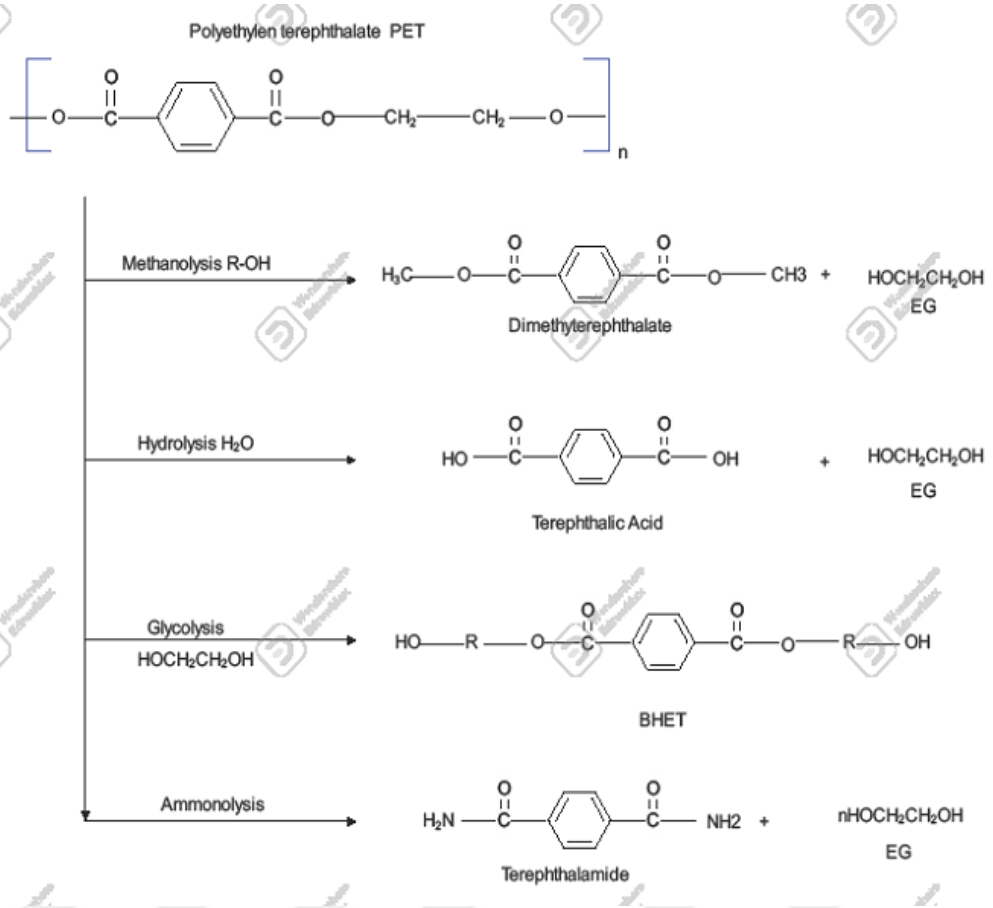


Figure 1.5 Depolymerization types of PET (Raheem *et al.* 2019a)

1.6.1 Glycolysis

Due to its low reaction temperature and low volatility of reagents (e.g., EG, diethylene glycol DEG), glycolysis of PET is one of the earliest and simplest processes employed for industrial-scale PET recycling around the world. At temperatures between 170 and 300 ^{o}C, Oligomers like bis-hydroxyethyl terephthalate (BHET) with two terminal hydroxyl groups are produced through the transesterification of PET with an excess quantity of glycol (Siddiqui *et al.* 2021). The procedure entails a transesterification reaction of PET with an excess of glycol, which encourages the synthesis of BHET (2-hydroxyethyl terephthalate). In the partial hydrolysis of the PET with EG, the BHET monomer and a low-molecular mixture of oligomers can be recycled to the PET synthesis procedure or used to create a variety of polymers, including unsaturated polyesters, polyurethanes, vinyl esters, epoxy resins (Geyer *et al.* 2016). see Figure (1.6).

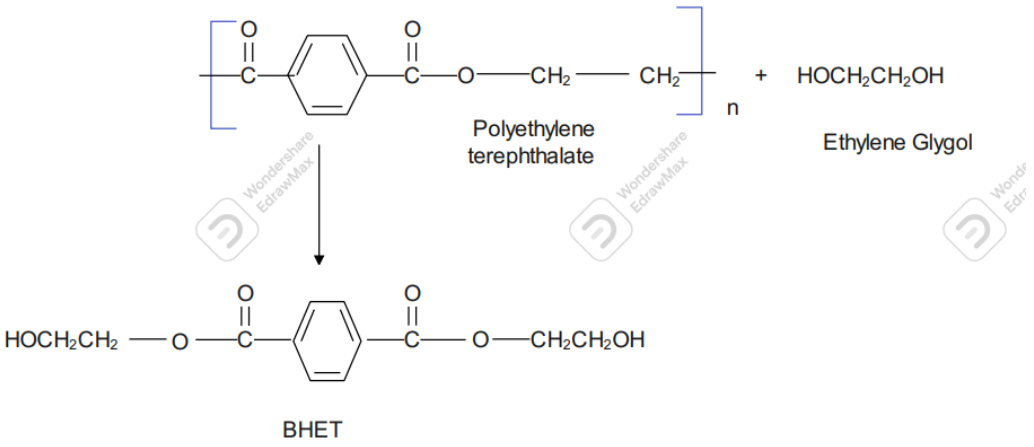


Figure 1.6 Glycolysis reaction oF PET (Raheem *et al.* 2019a)

1.6.2 Methanolysis

The most popular alcoholysis process, methanolysis of PET, can be carried out using any one of three types of methanol: liquid (standard), super-heated (vapor), or supercritical (Shojaei *et al.* 2020). Dimethyl terephthalate (DMT) and ethylene are the major products of methanolysis, which is the breakdown of PET by methanol at high temperatures and high pressures (Pudack *et al.* 2020). Dimethyl terephthalate (DMT) and ethylene glycol (EG), the basic material used to make this polymer, are the primary byproducts of PET methane analysis (Products 2022), catalysts that interact with lead dioxide, cobalt acetate, and zinc and magnesium acetate Zinc acetate is the catalyst that is most commonly used. Methods for delivering methane breakdown Similar fundamental variations include, for instance, 180–280 °C and pressures of 2-4 Mpa (Pham and Cho 2021). In comparison to a liquid technique, superheated vapor methanolysis uses less pressure to carry out the transesterification reaction. This process uses vapor methanol rather than liquid methanol and operates at a lower pressure than liquid methanolysis, which results in a slower rate of decomposition. However, the equilibrium will be disturbed and the reaction will shift toward larger yields since the reaction product (vaporous DMT) exists (Kim *et al.* 2008). Recently, PET methanolysis has been carried out using supercritical methanol at a temperature of 300^{o}C and a pressure of more than 80 atm. The depolymerization of PET has drawn attention to the

reactivity of supercritical methanol. at its critical point, the supercritical fluid has a high density similar to that of a liquid and a high kinetic energy similar to that of a gas molecule. When using these conditions, PET decomposition proceeded significantly more quickly than when using liquid methanol, see Figure (1.7) (Han 2019).

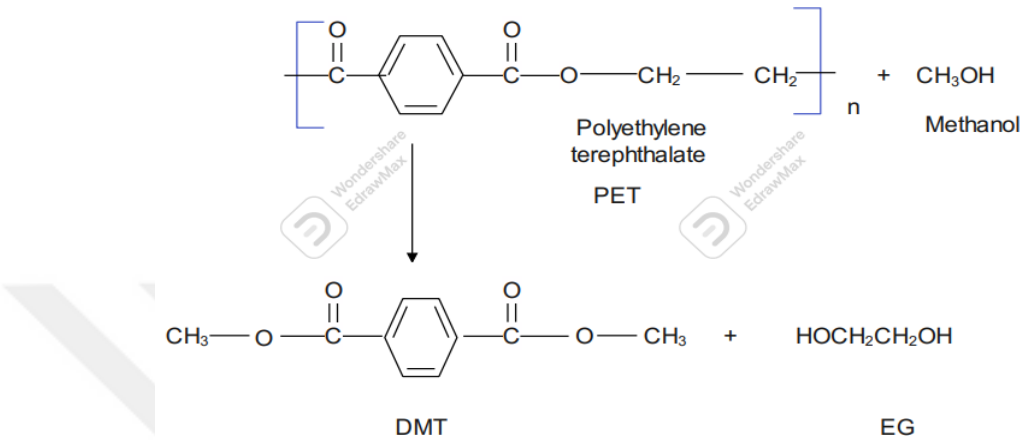


Figure 1.7 Methanolysis reaction of PET (Han 2019)

1.6.3 Aminolysis

Recycling PET with a variety of primary amine solutions, including methylamine, ethylamine, ethanolamine, allylamine, and hydrazine, is known as the aminolysis of PET. accordingly causing the creation of TPA and EG diamides in aqueous form. Alcohols have a slower effect on polymer degradation than organic bases called amines (aminolysis) (Raheem *et al.* 2019b). The partial aminolysis process has been applied for property enhancement in the production of PET fibers. It is reported that the polymer is taken either in the form of powder or fibers. The range of temperatures is between 20 and 100 ^{O}C. At lower temperatures of 21^{O}C, primary amines, and anhydrous n-butyl amine were used as analytic agents. the fundamental stearic hindrances (size) and the type of an amine about water control the aminolysis rate of PET degradation (Wakabayashi *et al.* 2012). Utilizing complex amines such as EG and the related mono- and diamines of TPA, such as N, N1-Dialkyl Terephthalate (Alkyl amine), N, N1-Dialkyl Terephthalate (Allyl amine), BHETA (Ethanol amine), Terephthalohydroxamic

Acid (Hydroxyl amine hydrochloride), Terephthalic Dihydrazide (Hydrazine hydrate), Bis (Ethylene diamine), see Figure (1.8) (Raheem *et al.* 2019b).

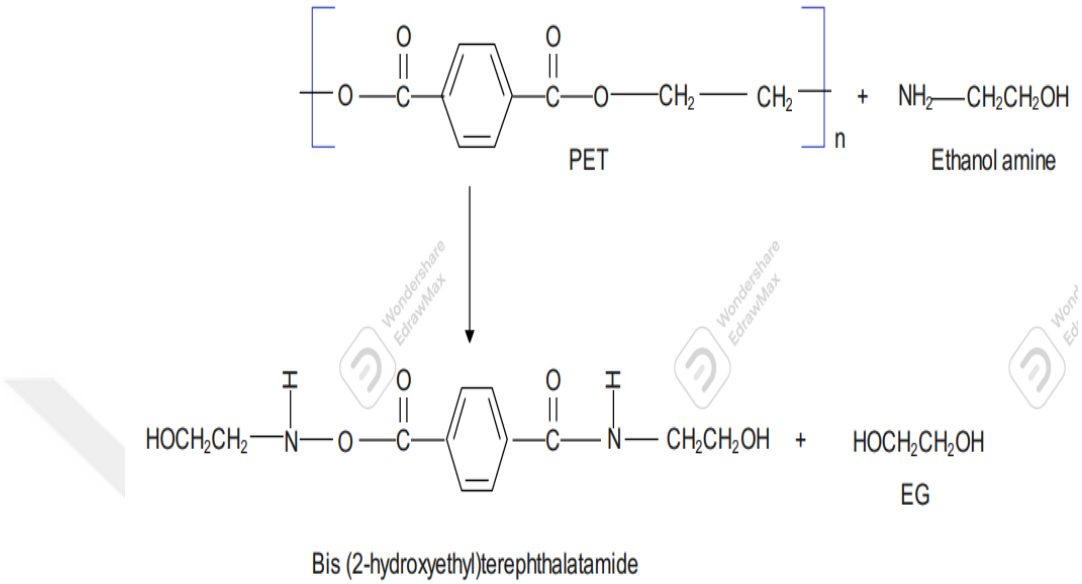


Figure 1.8 Aminolysis reaction of PET (Han 2019)

1.6.4 Ammonolysis

It involves the breakdown of PET materials with ammonia (NH3) at pressure and temperatures between 70 and 180 ºC. PET bottle waste can be safely digested for 1–7 hours with an appropriate catalyst, such as zinc acetate (0.5%), to produce terephthaldiamide (TPA di-amide) and EG. These conditions are (120–180)ºC and 2 MN/m2 (low pressure can also be utilized) (Al-Sabagh *et al.* 2016).

TPA di-amide is a middle product used to create terephthalonitrile, which can then be hydrogenated (H) to create p-xylylene diamine or 1, 4-bisterephthalonitrile (amino-ethyle) PET trash in EG medium is treated with anhydrideammonia to create TPA amide (Lorenzetti *et al.* 2006). TPA amide is a potential precursor to terephthalonitrile, which can then be used to make p-xylylene diamine or 1, 4-bis(aminoethyl) cyclohexane, see Figure (1.9) (Benyathiar *et al.* 2022)

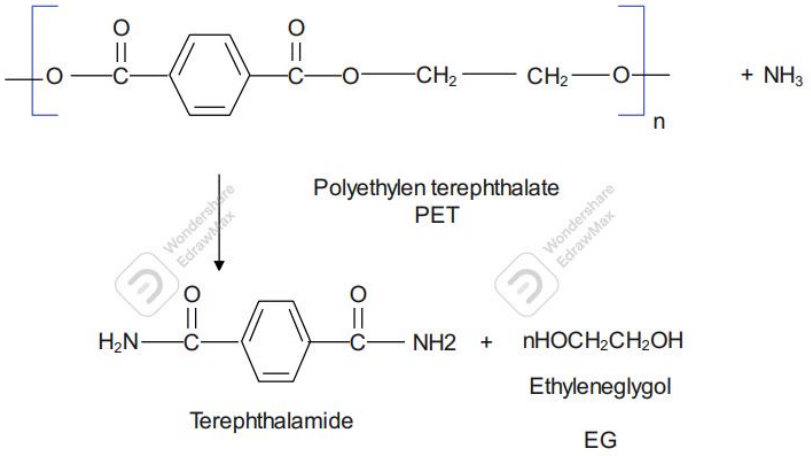


Figure 1.9 Ammonolysis reaction of PET (Han 2019)

1.6.5 Hydrolysis

The purpose of hydrolysis is to create(TPA and EG) monomers. (EG) and (PET) can be hydrolyzed to create the monomers TPA and EG in an acidic, alkaline, or neutral environment. The creation of a new element for the direct synthesis of PET from TPA and EG is related to the rising interest in this technology. There are three types of hydrolysis for PET: neutral, acidic, and alkaline (Sinha *et al.* 2010).

1.6.5.1 Neutral hydrolysis

Neutral hydrolysis is the process of depolymerizing PET using water or steam without the addition of an acid-base catalyst. It typically takes place at a temperature of 250–300 °C and a pressure of 1.5–4.0 Mpa. Water and reaction feed PET typically weigh between 1:2 and 1:12 of each other. PET can be immediately depolymerized into monomers for the synthesis of polyester using the neutral hydrolysis process without the creation of an acid-base waste liquid (Sinha *et al.* 2010, Cao *et al.* 2022). The great ecological purity of neutral hydrolysis is without a doubt a benefit, and as a result, it is reasonable to predict that interest in this technology will increase. The TPA's disadvantage is that it retains all mechanical imperfections that were present in the polymer, giving the end product a much lower purity than that of acid or alkaline

hydrolysis (Al-Sabagh *et al.* 2016). Traditional catalyst systems, like metal salts, are added to neutral hydrolysis to speed up the reaction. However, because there are so many metal ions in the reaction media, it is challenging to separate them after the reaction, which lowers the TPA purity of the final product. TPA can enter the layered hydroxide and is simple to separate from the mixed liquid thanks to the layered hydroxide's good anion exchange characteristics and great affinity for terephthalate ions (Cao *et al.* 2022).

1.6.5.2 Acidic hydrolysis

In this method . Mineral acids such as nitric or phosphoric acid have been used, and concentrated sulfuric acid is the most commonly used for acid hydrolysis. To prevent the reaction from being exposed to excessive pressures and temperatures**.** Although this process often gives good yields, a significant downside is the separation of the EG from the extremely acidic solution. In addition, the quantity of acid required to industrialize this process creates issues for the environment, processes, and the economy (Dutt and Soni 2013).

1.6.5.3 Alkaline hydrolysis

An aqueous alkaline solution of sodium hydroxide (NaOH) or potassium hydroxide (KOH) is used to perform alkaline hydrolysis. Over some time, the process takes place at temperatures up to 250 degrees Celsius and certain pressures. Sodium disodium or dipotassium terephthalate is produced as a result of this reaction. , and the TPA is separated from it by treating it again with acidic acid (Benyathiar *et al.* 2022). The alkaline depolymerization kinetics of PET in an alkaline solution depend on several variables, including temperature, time, alkaline concentration, and catalyst concentration. (Shojaei *et al.* 2020)As a way to chemically recycle PET and recover a high yield of pure terephthalic acid, PET hydrolysis in an alkaline solution while being microwaved was examined. When compared to conventional heating, the use of a microwave enables an incredibly fast reaction time for completely degrading PET waste

and warming at high-quality heating that does not come into contact with the material being heated see Figure (1-10) (Căta *et al.* 2017).

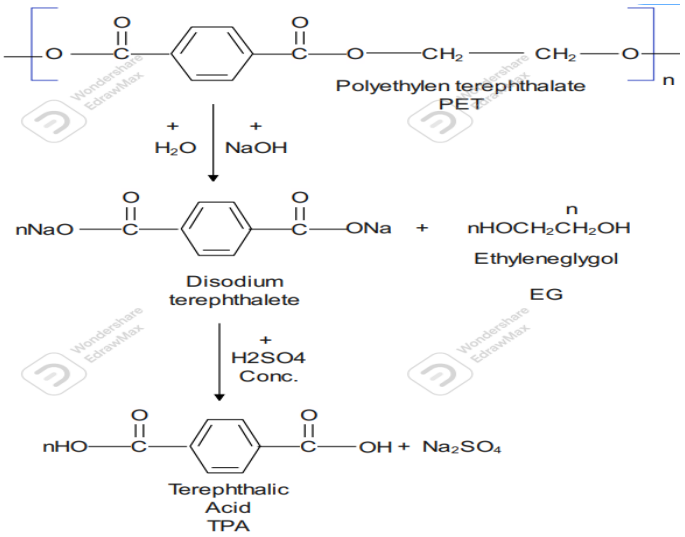


Figure 1.10 Alkaline hydrolysis reaction to creat TPA (Han 2019)

The hydrolysis of PET occurs via the following chemical pathway: The presence of an alkoxide base (CH_3O) in the first phase of the reaction causes an ester exchange reaction, which attacks the electron-deficient carbonyl carbon, creating an intermediate anion with the possibility of reversing the process or forming the product. The ester carbonyl center is attacked by hydroxide ion (OH) again in the second step of the reaction to generate the sodium salt of TPA, which is not further attacked by any base and the reaction is irreversible. As a result, the reaction proceeds to completion in the direction of hydrolysis (Mohsin *et al.* 2018,Wan *et al.* 2001).

1.7 Micro Wave Irradiation

In comparison to traditional heating techniques, microwave irradiation has various benefits, including noncontact, immediate, and quick heating with high specificity. As a result, it is a commonly used technique for heating and drying materials and is applied in several domestic and industrial settings (Pingale and Shukla 2008,Tierney and Lidström 2009). The fundamental benefit of adopting microwave heating over conventional heating is that because the molecules in the reaction mixture are directly

associated with the microwave energy, the temperature rises quickly yet remains under control (Siddiqui *et al.* 2010). The two primary processes for transferring energy from microwave irradiation to the reacting molecules are dipole rotation and ionic conduction. Polar molecules and the electric field component of microwave radiation interact through dipole rotation; as polar molecules align with the microwave's rapidly shifting electric field, energy is transferred. Polar solvents that can directly absorb microwave radiation include water, methanol, ethanol, acetone, and dimethylformamide. This significantly speeds up the reaction rate of the dissolved reagent. However, if free ions or other ionic species are present in the reaction mixture, ionic conduction occurs. Under the influence of an electric field, the free ions travel through the solution, causing an energy expenditure due to an enhanced collision rate that converts the kinetic energy to heat. When it comes to the ability to generate heat, the conductivity mechanism interacts with the system considerably more strongly than the dipolar mechanism (Wang and Mao 2012, Mohsin *et al.* 2018).

1.8 Alkaline Hydrolysis in the Presence of a Phase Transfer Catalyst

Several of the most long-lasting catalysts are made of metallic oxides, such as titanium dioxide. Heat stability, light stability, chemical inertness, lack of bleeding and migration, appropriate electrical characteristics, and low absorption are among the benefits of these materials. Zinc oxide can also be used. The following are the typical qualities of titanium dioxide shown in Table (1-1) (Salminen 2013).

Table 1.1 Properties of typical qualities of titanium dioxide (Salminen 2013)

Poroperties	**Anatas**	**Rultile**
Avarage Partical size (μ)	0.3	0.2-0.3
Density (g/ cm^3)	3.9	4.1
Refractive Index	2.55	2.76
Tinting Strength	1200	1600
Oil Obsorption(Ib/100Ib)	18 - 30	16-48
Hardness (Mohs)	5-6	6-7

The titanium oxide must be eliminated during the depolymerization reaction if the recovered monomers are pure and identical to conventional ones. Due to the small size of the oxide crystals, the removal of titanium dioxide is an essential step (generally, greater than 0.2 M). Titanium oxide upon depolymerization may cause opacity of the polymer, which deteriorates the properties of the recycled monomer products (Crippa and Morico 2019).

Theoretically, it might be possible to use the same catalyst to efficiently catalyze two reactions because ethylene glycol depolymerization and PET condensation processes are essentially transistor working processes. However, it is difficult to produce efficient and directional catalysis of two reactions by a single component at the same time due to the different roles played by different metallic elements in stimulation. If several catalytic processes are combined into a single catalyst at once, the activity of titanium-based catalysts can be changed by changing the coordination number and the bonding structure (Cao *et al.* 2022).

1.9 Problem Statement

Problem: The development of an efficient and sustainable method for the depolymerization of post-consumer PET plastic waste to yield high-quality monomers for the production of new PET products.

Explanation: PET (polyethylene terephthalate) is a widely used plastic for packaging materials, clothing fibers, and other products due to its durability, transparency, and resistance to moisture and chemicals. However, the accumulation of PET waste in the environment poses a significant challenge to waste management and sustainability. The depolymerization of PET into its constituent monomers (terephthalic acid and ethylene glycol) can enable the recycling of PET waste into new products, reducing the need for virgin PET production and minimizing environmental impacts. Current depolymerization methods involve harsh conditions and high energy consumption, leading to low yields and poor quality of the monomers. Therefore, the development of an efficient and sustainable method for PET depolymerization is crucial for realizing the

potential of PET recycling. The problem statement focuses on addressing this challenge by investigating novel depolymerization methods that can achieve high yields of high-quality monomers from post-consumer PET waste.

The Aım of Study:

1. Contribute to finding solutions to environmental problems represented by the accumulation of plastic waste
2. Recovering part of the economic value by making use of (PET) waste and converting it into raw materials
3. Developing and improving the alkaline hydro depolymerization process using an irradiator, NAOH alkaline material, and a titanium dioxide catalyst.
4. Estimating and analyzing the results obtained from the experiments, such as (TPA purity) and the amount of (transformed PET).
5. Updating the variables affecting the depolymerization in order to facilitate and simplify the process and make it more efficient, such as reducing the temperature, decreasing the alkaline solution concentration , decreasing the amount of catalyst, and decreasing the process time.

2. LITERATURE REVIEW

In recent years, it has been noticed that research on this subject has increased significantly, and for this reason, in this section, literary research was conducted on the subject of the thesis, and studies were taken on the same subject as closely related to it as possible.

2.1 Hydrolysis Study

By hydrolysis, PET can be depolymerized into EG and TPA. Due to the high cost of purifying the recycled TPA, hydrolysis is not frequently employed for recycled food-grade PET. Under acidic, basic, or neutral conditions, this process can be carried out at high pressures of (1.4–2) MPa and high temperatures of (200–250) °C. The following are some of the studies on hydrolysis techniques (Benyathiar *et al.* 2022).

Islam *et al.* (2023), by using a sintered glass filter, terephthalic acids (TPAs) were removed from the reaction mixtures. Before using it in a later batch of PET depolymerization, the viscosity of the recycled hydrolysis fluid was evaluated as the viscosity of the hydrolysis fluid was gradually increased from 5 mm^2/s to 87 mm^2/s. The yields of TPA ranged from 85.03 % to 99.20 %, and in the last batches, the color of TPA turned from bright white to off-white (Islam *et al.* 2023).

Because of the quantity of metal ions that act as catalysts, Dorin Stanica-Ezeanu and Danuta Matei suggested that marine water is a perfect reactor. The experimental data was overlaid with a first-order kinetic model. The activation energy was calculated to be 73.5 kJ/mol, and the exponential factor was 5.33107 h^{-1}. The mathematical model answer demonstrates that in the tropics, 100% PET conversion takes just 72 years and 50% PET conversion takes only 4.5 years because the entire ocean is a massive batch reactor operating under isothermal circumstances (Stanica-Ezeanu and Matei 2021).

In this study, the depolymerization of polycarbonates (PC) and polyethylene terephthalate (PET) in separate and mixed streams was investigated. The low-cost KOH-in-methanol (KMH) hydrolysis method designed for immediate PET hydrolysis allows selective depolymerization of (PET) and polycarbonate (PC) blended streams as well as single-step separation of monomers with exceptional energy efficiency. Separation of bisphenol A and TPA in one step has been demonstrated (Rubio Arias *et al.* 2022).

In this study, Zhang *et al.* (2022), established mild non-aqueous hydrolysis for easy product separation and selective ester cleavage of PET. For the production of terephthalate by hydrolysis in the presence of KOH, this work uses ethylene glycol (EG), specific for the polymerization of PET, and tetrahydrofuran (THF). In addition, THF had an activating effect on the hydroxyl group of EG, synergizing. The reaction between potassium hydroxide and alkoxide caused the ester bonds to break in PET (Zhang *et al*. 2022).

Yang *et al.* (2021) used an acid catalyst to enhance the hydrolysis of PET, and a TPA yield of 95.5% was achieved under ideal conditions. A high purity of 99%, compared to fresh TPA was also demonstrated by the generated TPA, and it was It is easy to recover for PET hydrolysis without laborious labor and purification procedures, and the hydrolysis efficiency remained constant during eight consecutive reaction cycles. Overall, this work provides a safe, simple, and affordable method for TPA production (Yang *et al.* 2021).

With a reaction time of 1 to 30 minutes, the studies were conducted in a batch reactor at temperatures ranging from 250 to 400 °C. There were primary and secondary products created during the hydrolysis of PET waste. the yield was seen from colorless PET trash and (85.0 ± 0.2%) from green PET waste. The final TPA made from PET trash was almost entirely pure (Čolnik *et al*. 2021).

Cong-hao *et al.* (2018), in this study, they optimized the effects of different experimental conditions on the depolymerization of waste PET bottles by using the

alkaline-alcohol hydrolysis method to depolymerize waste PET bottles. The results of the optimization tests show that the reaction temperature, reaction time, sodium bicarbonate to PET mass ratio, and water volume to PET mass ratio are ideal conditions. It is expected that the use of this alkaline-alcohol hydrolysis technology combined with alcohol hydrolysis and hydrolysis will provide an effective long-term recycling method for used PET bottles (Cong-hao *et al.* 2018).

The post-consumer depolymerization reaction of PET was performed with NaoH concentrations. At a concentration of 7.5 mol L NaOH, the reaction was also performed with differently colored PET, but the results were not as successful as those obtained with uncolored PET. The problem may be colorants, which, due to their chemical structure, compete with the hydroxyl ion (OH- for nucleophilic attack during the hydrolysis reaction of PET (Dos Santos *et al.* 2018).

Mohsin *et al.* (2018), the in situ hydrolysis of polyethylene terephthalate (PET) with sodium methoxide in methanol and dimethyl sulfoxide (DMSO) as the solvent was explored to produce terephthalic acid (TPA). The reaction was performed with the help of a microwave between 5 and 30 minutes, at different temperatures. It was found that the amount of sodium methoxide, volume of methanol and DMSO used, reaction time, and temperature all have a significant effect on the reaction (Mohsin *et al.* 2018)

Kosmidis *et al.* (2001),studied how temperature, alkali concentration, PET concentration, PET particle size, and catalyst-to-PET ratio affected TPA yield. Temperature (70-95) °C, NaOH content (5-15 wt%), average particle size, catalyst, and PET concentration were just a few of the reaction kinetics parameters investigated. and Using NaOH to produce high-purity terephthalic acid. TPA in the H NMR spectrum showed a mixture of isophthalic acid and 98% purity of terephthalic acid (Kosmidis *et al.* 2001).

Ügdüler *et al.* (2020), PET with the highest yield was depolymerized at 80 °C with a particle size of less than 500 μm in a solution containing (60: 40 vol.% ETHANOL: H2O, 5 wt.% NaOH , and at 80 °C)in 20 min. As expected, an increase in temperature

and a decrease in particle size lead to a higher diffusion model for PET depolymerization that adequately describes the kinetic behavior of the alkaline hydrolysis of PET (Ügdüler *et al.* 2020).

Azeem *et al.* (2022),have depolymerized by green and rapid hydrolysis of polyethylene terephthalate (PET) under microwave radiation (MW) with excellent efficiency. The catalytic activity of two deep eutectic solvents (DES) based choline chloride-urea (DES 1) and choline chloride-thiurea (DES 2) was evaluated and compared in the MW-assisted glycolysis of PET. After glycolysis was performed, residual PET was produced, and depolymerization was carried out using MW-assisted hydrolysis in the presence of EG and weak base Na_2CO_3 (Azeem *et al.* 2022).

Attallah *et al*. (2021), using a solution/degradation strategy designed for mechanically interlocking polymer relationships, depolymerized waste PET bottles. By adjusting the volume of the deep eutectic solvent (DES), the concentration of the depolymerizing agent (NaOH), and the irradiation period in MW as independent variables, the PET depolymerization was optimized using a Box-Behnken design. Due to the excellent physical and chemical properties of DES, straightforward and affordable purification procedures can be used to produce terephthalic acid (TPA) monomers with respectable yields (Attallah *et al*. 2021).

Myren *et al.* (2020), using caustic solutions with high concentrations of NaOH, demonstrated the feasibility of an innovative and environmentally friendly technique for the electrochemical recycling of end-use PET based on inexpensive solvents (water and methanol) and reagents (NaCl and electrolyte) When PET was depolymerized in a methanol reflow with the addition of NaOH and 75% terephthalic acid, yields of up to 65% were seen after only 40 minutes of microwave irradiation at 85 °C (Myren *et al.* 2020).

Kandasamy *et al.* (2020), found that by chemically recycling the PET waste in the reactor, this procedure results in the complete depolymerization of PET into its monomers, and at 90°C, 92% of the PET will be converted. PET bottles are chemically

recycled from post-consumer waste using alkaline hydrolysis. To increase reaction efficiency, process parameters, including time, temperature, ethylene glycol, and catalyst concentrations, are changed (Kandasamy *et al.* 2020).

Wang and Mao (2012), used an excess of methanol, ethanol, 1-butanol, 1-pentanol, and 1-hexanol in the presence of several simple basic catalysts, namely potassium hydroxide, sodium hydroxide, sodium acetate, and zinc acetate, and hydrolysis with the help of a microwave reactor is described. Poly(ethylene terephthalate). Except for ethylene glycol oxidation, the reactions took place quickly and without any adverse effects. Terephthalic acid and ethylene glycol with potassium hydroxide have been produced in their purest form and with suitably high yields (Wang and Mao 2012).

Mukrimaa *et al.* (2016), investigate depolymerized PET in aqueous NaOH solution in a batch process with a range of PET particle sizes ranging from 50-512.5 μm. The desired reaction time and PET particle size were set. PET concentration and NaOH concentration were the first orders of rate of the depolymerization reaction. The value of TPA varies with the reaction time. This indicates that EG and disodium terephthalate are produced as a result of the simultaneous hydrolysis of PET molecules and aqueous NaOH (Mukrimaa *et al.* 2016).

Arias and Thielemans (2021), suggested that PET can be converted into TPA with the help of a microwave. The higher efficiency of this procedure over other reported hydrolysis methods using depolymerization kinetics was evaluated and found to result from a thicker shrinkage layer. Our ability to obtain dimethyl terephthalate (DMT) through the use of an anhydrous depolymerization system that can convert PET to DMT but requires careful moisture control is made possible by evidence of the increased reactivity of free OH species (Arias and Thielemans 2021).

Liu *et al.* (2014) explored the microwave-aided catalytic neutral hydrolysis of PET. The effect of the principal reaction variable on the degree of depolymerization was investigated. A set of acidic ionic liquids, including N-methylimidazolium hydrogen sulfate([Hmim][HSO4]), 1-Ethyl-3-methylimidazolium hydrogen sulfate

([Emim][HSO4]), 1-butyl-3-methylimidazolium hydrogen sulfate ([Bmim][HSO4]), and 1-hexyl-3-methylimidazolium hydrogen sulfate ([hexanemim][HSO4]) were prepared as catalysts. According to the data, [hexanemim][HSO4] had the highest catalytic efficiency. The greatest degree of depolymerization was obtained with a catalyst quantity of 0.01 mol/2 g PET, a reaction time of 210 minutes, and a reaction temperature of 195 degrees Celsius (Liu *et al.* 2014).

Khalaf and Hasan (2012),PET was depolymerized using the open-vessel technique and microwave irradiation. 0.5 mm of PET, 10% NaOH, and microwave irradiation at 200 watts with quaternary ammonium salt were used as phase transfer catalysts (PTC). At the level of depolymerization, the effects of irradiation time, baseline concentration, particle size, amount of PTC, and microwave radiation power were investigated. The results indicate that 10% NaOH, 60 minutes, 200 watts of power, and 3% wt./wt. PTC/PET were in very good condition to produce TPA (Khalaf and Hasan 2012).

Căta *et al.* (2017), in this study, they focus on the high-yield of terephthalic acid from PET waste using microwave irradiation and alkaline hydrolysis. The disodium salt of TPA, the primary product, is converted to TPA through acid treatment. To find the ideal conditions under which the reaction is completed, the effects of reaction time, temperature, and volume of the alkali solution on TPA yield were studied (Căta *et al.* 2017).

DEMETO technology (Modular, Scalable, High-Performance Depolymerization by Microwave Technology) claims a reaction time of 10 minutes to complete the depolymerization of PET flakes, at minimal pressure and temperature. PET flakes, powders or fibers are fed into the DEMETO depolymerization process. 1 mole of a repeat unit of PET yields 1 mole of the intermediate sodium terephthalate and 1 mole of ethylene glycol (Crippa and Morico 2019).

There is no study with TiO_2 as a catalyst in alkalin hydrolsis but there are many studies with powdered PET with not representative real situations as there are few studies on microwave ovens and very few studies on experimental design.

3. MATERIALS AND METHODS

Information regarding materials, tools, and the experimental setup are the main topics in this chapter. In addition, the tools used to analyze samples collected for PET depolymerization are explained in detail, along with their mode of operation. In our work, the alkaline hydrolysis depolymerization of PET waste in an alkaline solution using a microwave irradiation heating technique was investigated to obtain pure terephthalic acid with a high yield.

It's possible to use Taguchi's design to put data and variables (temperature, time, amount of TiO2, and concentration (NaOH) wt/vol). We also used ANOVA (Analysis of Variance) to determine if there was a statistical difference between groups. The test showed that all parameters examined were effective.ANOVA was used to check the effect of four different experimental conditions (temperature, time of experiment, concentration of NaOH solution, and amount of catalyst) on the amount of transduced PET.ANOVA and Taguchi's data were analyzed using Minitab software.

3.1 Methology

Dr. Genichi Taguchi devised an entirely new experimental method in the 1940s called the Taguchi Technique, which uses a modified, standardized method for designing tests. To analyze a large number of variables with a minimum number of tests, Taguchi's technique uses orthogonal matrices. The number of experimental parameters can be significantly reduced by using orthogonal matrices. Moreover, the results of a limited number of experiments are applicable to the entire experimental field, which reduces research and development expenses by simultaneously analyzing a large number of experimental variables. Taguchi's approach can be used to optimize the process parameters such as reaction time, temperature, catalyst type or amount, etc (Park *et al.* 2020).

3.2 Experimental Parameters Range

It is necessary to choose the optimal conditions for conducting any research work, and after knowing the conditions and factors influencing the course of the experiment, these conditions were determined, namely temperature, concentration, amount of catalyst, and time. After making many trials to find the best conditions to give the best results, periods, ratios, and quantities were determined Variables were obtained to remove the polymerization up to 100% with very high purity and using low-cost materials The following Table (3.1) shows the variables with the values used in the experiments.

Table 3.1 Variables of effects used in the experiments

parameters	values
Temperature	(165,180 ,195) ^{O}C
NaOH concentration	(4,8,12) % weight/volume
TiO_2 amount	(0.01,0.02,0.03)g
Time	(10,20,30) minutes

By using the Taguchi method It was decided that the parameters should be 3 levels and 4 factors the factor is (temperature, time of reaction, concentration of alkaline solution, and catalyst amount)and the levels are for temperatures (165,180,195) ^{O}C for alkaline concentration (4,8,12)% weight/volume, TiO_2 catalyst amount (0.01,0.02,0.03)g and time of reaction are (10,20,30) minutes.

For that, the full factorial design, $3^4 = 81$ experiments are required The Taguchi $L93^4$ orthogonal experimental designs are selected see Table (3.2), and 9 experiments are required in this design experiments we decided to repeat each experiment four times. A total of 4x9=36 experiments were done the Table (3.3) show Taguchi L9 3^4 orthogonal experiment design with symbolic values.

Table 3.2 Taguchi L9 3 4 orthogonal experiment design with symbolic values

Experiment number	Temperature (°C)	Time minutes	KOH concentration (%wt./ vol.)	Catalyst TiO_2amount
1	1	1	1	1
2	1	2	2	2
3	1	3	3	3
4	2	1	2	3
5	2	2	3	1
6	2	3	1	2
7	3	1	3	2
8	3	2	1	3
9	3	3	2	1

Table 3.3 Taguchi L9 34 orthogonal experiment design with actual values

Experiment number	Temperature (°C)	Time of reaction (min)	NaOH concentration (%wt./vol.)	Catalyst amount in gram
1	165	10	4	0.01
2	165	20	8	0.02
3	165	30	12	0.03
4	180	10	8	0.03
5	180	20	12	0.01
6	180	30	4	0.02
7	195	12	12	0.02
8	195	24	4	0.03
9	195	36	8	0.01

3.3 Analysis of Variance (ANOVA)

ANOVA stands for Analysis of Variance, which is a statistical technique used to determine whether there are significant differences between the means of three or more groups. ANOVA is used to test the null hypothesis that the means of all groups are equal.

To perform an ANOVA, you need to follow these steps:

1. Determine the number of groups you want to compare, and collect data on the variable of interest for each group.

2. Calculate the sample mean and sample variance for each group.
3. Calculate the overall mean and overall variance for all groups combined.
4. Calculate the between-group and within-group sum of squares.
5. Calculate the F statistic by dividing the between-group sum of squares by the within-group sum of squares.
6. Determine the p-value of the F statistic using a statistical table or software.
7. Compare the p-value to the significance level (usually 0.05) to determine whether to reject or fail to reject the null hypothesis.

If the p-value is less than the significance level, then there is evidence to suggest that at least one group differs significantly from the others, and you can perform post-hoc tests to determine which groups are significantly different from each other. If the p-value is greater than the significance level, then there is no evidence to suggest that any group differs significantly from the others.

There are different types of ANOVA tests, depending on the number of factors and levels involved. One-way ANOVA is used when there is one factor with three or more levels, while two-way ANOVA is used when there are two factors with three or more levels each. There are also more complex ANOVA tests such as mixed-design ANOVA and repeated-measures ANOVA. ANOVA is a powerful tool for comparing the means of multiple groups, but it is important to make sure that the assumptions of ANOVA are met before using the test. These assumptions include normality, homogeneity of variances, and independence of observations. Violations of these assumptions can lead to inaccurate results and should be addressed before using ANOVA (Henson, 2015).

3.4 Set of Reactor

The reactor is considered the most important part of the depolymerization process as it is the main factor in controlling the variables (temperature and time) and microwave power. Data is entered via the control panel as in the see Figure (3.1), where the reactor's temperature is entered and the time in which the depolymerization process takes place. It also shows the temperatures with time and the pressures inside the

containers. The reactor begins by drawing a graph line, and it is in three stages. The first stage is the heating phase, where temperatures increase. When the specified temperature is reached, the reactor begins to draw a straight graph, which is the period prescribed for depolymerization this phase is the second phase, while the third phase, occurs at the end of the time specified for removal, then the temperature drops dramatically see Figure (3.2). At the end of the reactor's work, the containers can be removed from the reactor to complete the rest of the experiments. It is better to leave these containers for a sufficient time until they cool well, and then they can be opened.

Figure 3.1 Control panel data

Figure 3.2 Control panel curve line

3.5 Chemicals and Materials

The Table(3.4) contain details about the chemicals and materials utilized in this work, including manufacture, purity, and some other criteria.

Table 3.4 Chemicals and materials used in Expremants

No.	Materials	Molecular formula	Purity	Specifications	origin supplier
1	distilled water	H_2O	99.5%	M.wt. :18 (g/mole) pH : 7	Ch.Eng. Dep.Lab., ÇANKIRI University
2	Sodium hydroxide	NaOH	97 %	M.wt: 40 (g/mole) Shape : small pellets pH value :>14	Merck compeny
3	Titanium dioxide	TiO_2	99.5%	M.wt:79.866(g/mole) White to slightly coloured powder	From PubChem company
4	Hydrochloric acid	HCl	35-37 %	M.wt**:** 36.46 g/mol Colorless, transparent liquid, fuming in air	Merck compeny
5	Phenolphthalein	$C_{20}H_{14}O_4$	99%	White powder M.wt: 318.33g/ mole PHvlua: 8.3-10	BDH chemicals poole England
6	Poly ethylene terephthalate	PET	99%	particle size between (2-3) mm M.wt:89.500(g/mol)	Commercially available waste PET

3.6 Laboratory Equipment and Tools Used

The work was carried out inside the laboratory with devices and equipment, as we took into account the selection of the most appropriate devices, the lowest costs, the best performance,and high productivity.

3.6.1 Reactor

A Berghoff speed wave x-pert (Berghof, Germany) microwave reactor set was used. Berghoff DAK100 (manufactured from polytetrafluoroethylene PTFE or Teflon) reactors were used. microwave irradiation as compared with conventional heating

provides some advantages such as rapid heating with high specificity without contact with the material, shorter reaction times, great convenience, and reduced costs. A microwave reactor is a device that uses microwave radiation to carry out chemical reactions. It consists of a microwave generator, which produces electromagnetic waves at a frequency of around 2.45 GHz, and a reaction vessel that is capable of withstanding the pressure and temperature conditions required for the reaction see Figures (3.3,3.4,3.5) are shown the parts of the reactor. When the microwaves are directed into the reaction vessel, they cause the molecules in the reaction mixture to vibrate and rotate rapidly, which generates heat and can lead to faster and more efficient reactions compared to traditional heating methods. Microwave reactors are commonly used in organic chemistry and materials science for a wide range of applications, including the synthesis of new compounds, extraction of natural products, and degradation of polymers. They are particularly useful for reactions that are difficult or slow to carry out using traditional heating methods.

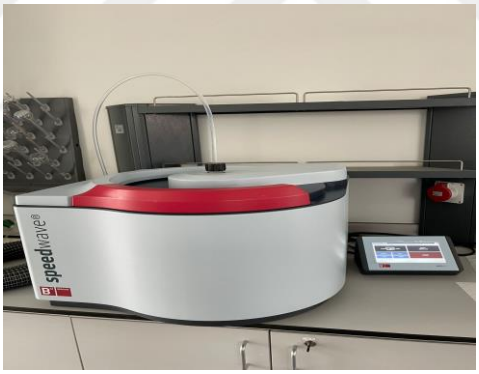


Figure 3.3 Reactor shape

Figure 3.4 Containers of reactor

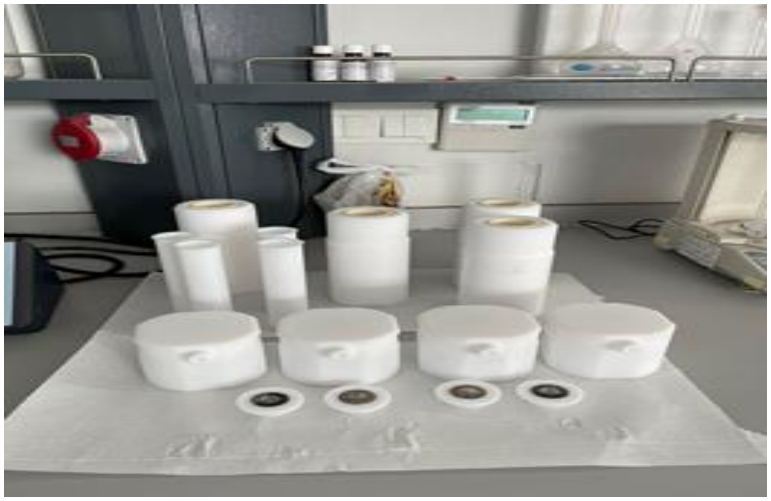


Figure 3.5 Teflon tubes

3.6.2 Fourir transform infrared (FTIR)

The reaction products were analyzed by using FT-IR spectroscopy(Bruker Tensor II ATR) used in our laboratory, FTIR spectroscopy is used to determine the characteristic chemical bond present in the TPA as well as the purified monomer. For studying the nature of chemical bonds present in the isolated compound, the IR spectra of TPA were taken after degradation processes and compared with the IR spectra for the standard. see Figure (3.6).

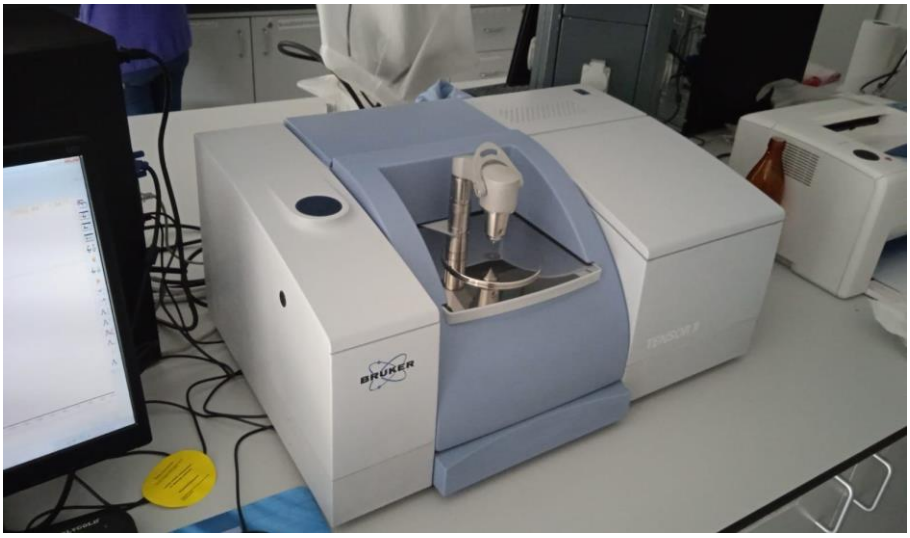


Figure 3.6 FT-IR spectroscopy device

3.6.3 1 H-NMR

In our study , we use 1 H-NMR Agilent Premium Compact Magnet: 14.1 Tesla (600 MHz Frequency) see Figure (3.7), 1 H-NMR (proton nuclear magnetic resonance) is a technique used to study the structure and properties of molecules in chemistry. The technique involves placing a sample containing hydrogen atoms (protons) in a strong magnetic field and then applying a radiofrequency pulse to the sample, causing the protons to absorb and emit electromagnetic radiation. The resulting spectrum shows the frequencies at which the protons resonate, which are characteristic of the chemical environment of the protons and can be used to identify the molecular structure.1 H-NMR devices typically consist of a strong magnet, a radiofrequency transmitter, and a detector, and are widely used in organic chemistry, biochemistry, and materials science for the identification and characterization of compounds.

Figure 3.7 1 H-NMR devic

3.6.4 Microscop

Scanning electron microscopy (SEM) is a type of electron microscope that obtains images by scanning the sample surface with a focused beam of electrons. Electrons interact with atoms in the sample, generating different signals containing information about the sample surface's topography and composition. we use electron microscopy

(Model: Sigma 300 VP) from the brand(Carl Zeiss) in our analysis work. See Figure (3.8).

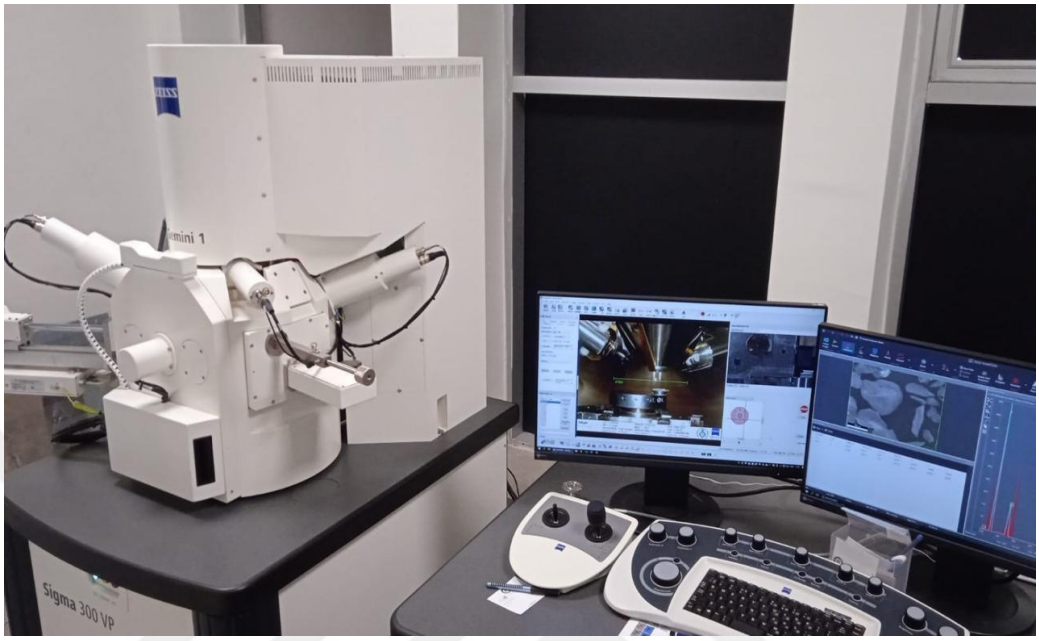


Figure 3.8 Scanning electron microscopy (SEM) device

3.6.5 Drier and balance

We use balance model(HR-250AZ) from AND company for measuring weight of materials. See Figure (3.9).

Figure 3.9 Balance device

The drier Model (JSOF/JSR) drying of PET slides and filter paper to dehumidify them at 70 °C and 24 hours in the hot air oven we used in our experiment, see Figure (3.10,3.11).

Figure 3.10 Drier from out side

Figure 3.11 Drier from in side

3.6.6 Sieves and laboratory tools

In our laboratory work, to obtain chips with a size ranging between 200 and 300 micrometers, a model sieve was used(Retsch Vibratory Sieve Shaker AS 200 basic) see Figure (3.12).

Figure 3.12 Sieves device

While conducting experiments in the laboratory, many laboratory materials were used, such as volumetric bottles and a glass beaker, as well as a graduated burette whose purpose was to neutralize basic solutions by adding HCL acid, as well as using Buechner in the filtration process, and it had a major role in the effective separation of TPA by filtration. see Figure (3.13, 3.14).

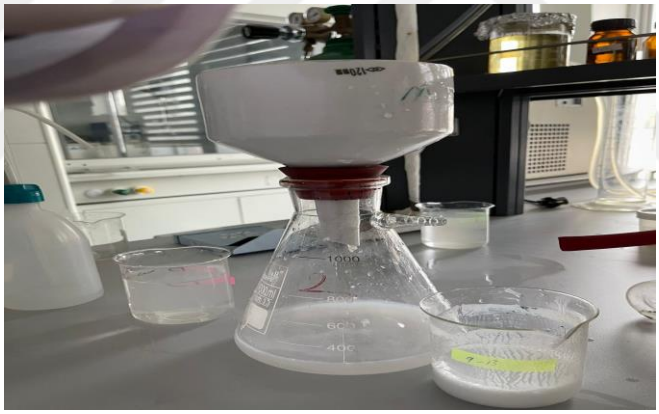


Figure 3.13 Buechner device

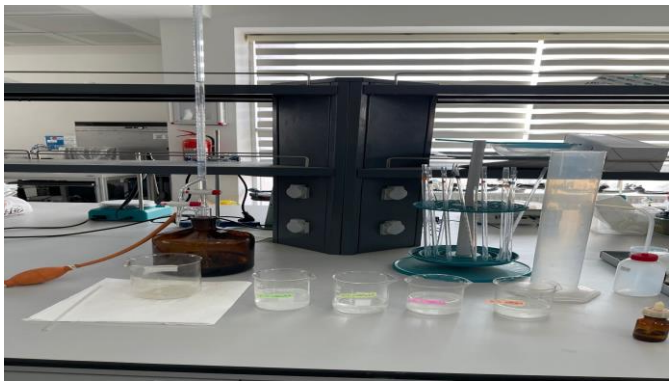


Figure 3.14 Laboratory tools

3.6.7 PH meter

In our work,we use a pH meter of the type (Mettler Toledo FG2-Basic FiveGo). A pH meter is an instrument that measures the acidity or alkalinity of a liquid or solution. It does this by measuring the concentration of hydrogen ions (H+) in the solution and converting that measurement into a pH value. see Figure (3.15).

Figure 3.15 PH meter

3.7 Experimental Procedure work

In this section, the laboratory work was divided into several sections in order to facilitate understanding and conducting these experiments:

1- Procedure Solutions preparation (NaOH,HCL and Phenolphthalein)
2- Procedure of preparation Titanium dioxide(TiO_2)catalyst
3- Procedure of PET PREPERATION
4- Procedure of PET treatment with Microwave reactor
5- Procedure treatment of product from microwave

The following diagram shows the events of the experiment from the beginning to the end of the experiment work, i.e. generating TPA. See Figure (3.16).

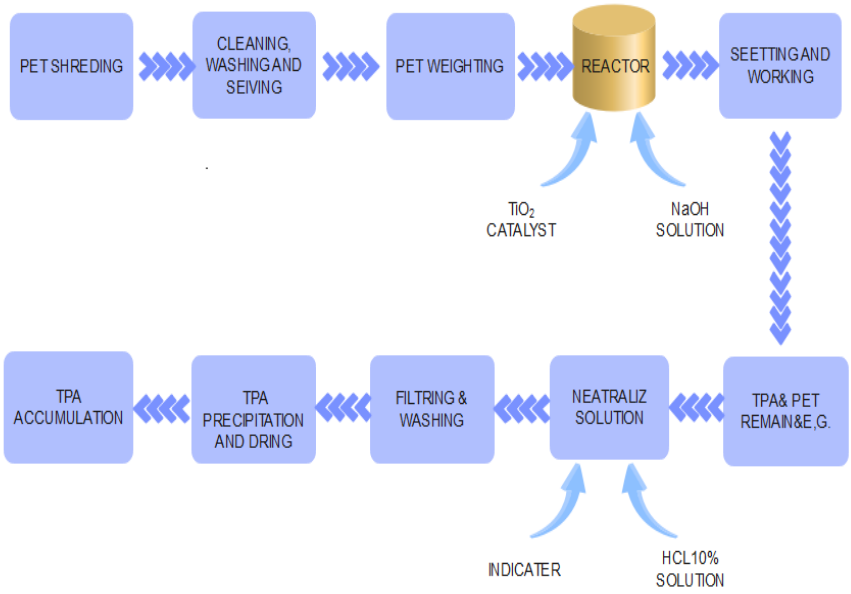


Figure 3.16 Experimantal work diagram

3.7.1 Procedure solutions preparation (NaOH,HCL and Phenolphthalein)

NaOH granules from Merck company were used to prepare three concentrations (4,8,12)% g/ml where one volume (30 ml) was added to all experimental samples. Sodium hydroxide solution is one of the main effects in the depolymerization process, as it is added to the reactor tubes with the catalyst and the PET. Figure (3.17), shows the effect of sodium hydroxide solution in the depolymerization process.

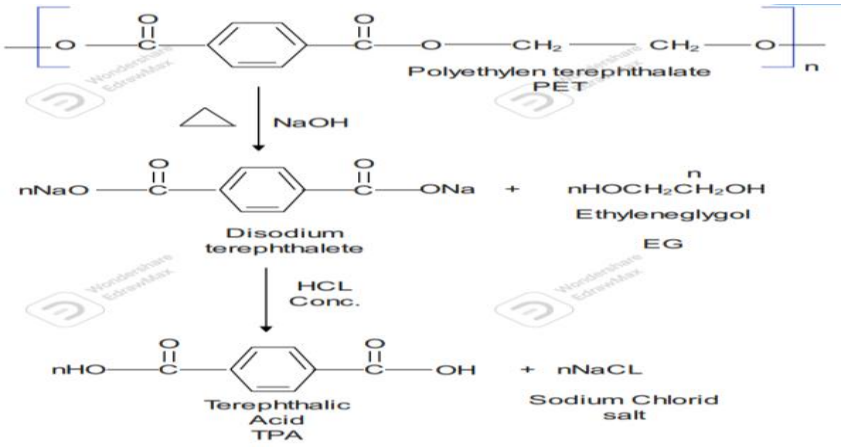


Figure 3.17 Depolymerization reaction of PET in alkaline solution

It is known to use one of the strong bases, such as concentrated sulfuric acid or hydrochloric acid, to neutralize basic solutions. In our experiments, concentrated hydrochloric acid from Merck was used to prepare 10% volume/volume, as 1000 ml was prepared by adding 100 ml of concentrated acid to water distilled in a volumetric bottle with a capacity of 1000 ml. Concentrated acid from HCl, which has a strong and pungent odor, was used to precipitate TPA from solutions, where it precipitates in the form of a white precipitate upon reaching pH = 2.

Using (Phenolphthalein) as an indicator for the neutralization of solutions, it was prepared by adding 50 grams of powder to water in a volumetric bottle with a capacity of 100 ml, to reach a concentration of 50%, Wt. / vol. The solution to be neutralized and taken from the reactor turns into a violet color when neutralized With 10% HCl acid when the indicator is added to the solution, it reaches approximately pH = 7.

3.7.2 Procedure of preparation titanium dioxide (TiO_2) catalyst

Titanium dioxide(TiO_2), which is a white powder, was used from a German facility from Merck as an auxiliary worker in the process of depolymerization, where three weights were prepared these weight of titanium dioxide is used as a catalyst factor in the process of depolymerization PET, where these weights were prepared which is (0.01,0.02,0.03) g, the catalyst added directly to NaOH solution and PET in the reactor tube.

TiO_2 is a commonly used catalyst in many chemical reactions and processes for several reasons.

1. High catalytic activity: TiO_2 has a high catalytic activity, which makes it effective in promoting chemical reactions.
2. Low cost: TiO_2 is relatively inexpensive compared to other catalysts, making it a cost-effective option.

3. Stability: TiO_2 is a stable and durable material, which makes it ideal for use in a range of chemical processes.
4. Non-toxic and environmentally friendly: TiO_2 is non-toxic and does not pose a risk to human health or the environment, making it a safe and environmentally friendly option.
5. Photocatalytic properties: TiO_2 is also known for its photocatalytic properties, which makes it useful in applications such as water purification, air purification, and solar energy conversion.

Overall, TiO_2 is a versatile and effective catalyst that can be used in a range of applications, including chemical synthesis, pollution control, and renewable energy production.

3.7.3 Procedure of PET preparation

PET is shredded commercially the PET using an industrial shredder. PET chips are made from old transparent PET bottles whose posters and adhesives were removed, as well as the isolation of large impurities and colors. The PET was shredded, which is of different sizes and uneven dimensions, and through the sieving process, and because the experiments are at a size ranging between (2000μm-3000μm), see Figure (3.18), and for this, you must obtain sufficient quantities of this size to be able to conduct experiments. After the sieving, the chopped PET with water is washed several times, to remove the dirt from the surface of the PET. The washed PET was put in the drier for 24 hours at 70 ^{0}C so that we have the PET prepared for the experiment.

It is well known that the more the surface space, the more the amount of the base in contact with it, and the more the area of the PET surface, the more the depolymerization process happens, and therefore it is important to know the size and removal the PET used in the experiments.

Figure 3.18 Shredded commercial PET

3.7.4 Procedure of PET treatment with microwave reactor

After preparing the sample from the PET chips and weighing it with a sensitive scale, the data entered into the reactor are determined from the temperature, the concentration of base added, and the weights of the catalyst, as well as determining the reactor time for work. The weight of PET is 2 g shown in Figure (3.19).

Figure 3.19 PET Weight

while the volume of the base solution (NaOH) is 30 ml in all experiments. The catalyst is added directly to the base solution with PET chips, and all materials are placed in a Teflon tube see Figure (3.20).

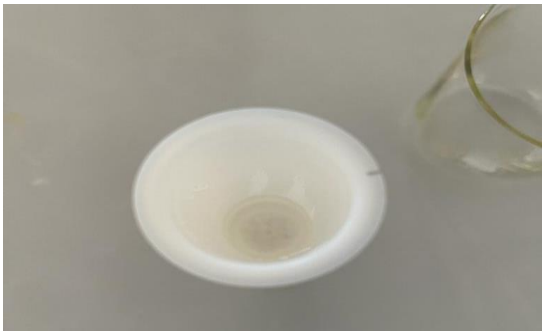


Figure 3.20 PET , Solutions and Catalyst in tube

And these tubes are placed in small containers that are closed tightly to prevent leakage from containers and there is ventilation for gases in the reactor , we choose four containers for all our experiments see Figures (3.21,3.22).

Figure 3.21 Tubes in containers

Figure 3.22 Cloosing containers

And these containers are placed oppositely inside the reactor, and they are connected well and tightly in the reactor, see Figure (3.23),The data is entered through the reactor control panel, as shown in Figure (3.24).

Figure 3.23 Containers in reactor

Figure 3.24 Control panel data

A graph line is drawn showing the course of the reaction occurring inside the reactor, where the temperature and time are shown as graphic line in the control panel screen look to Figure (3.25), as well as the pressure inside the containers can be expected indirectly, through a sensor. After the reactor is turned on, the reactor starts to rotate and the temperature rises above Through the microwave source, thus, the depolymerization

process begins, and the conversion of PET to TPA and ethylene glycol, the reaction progress can be followed by the line graph drawn in the control panel.

Figure 3.25 Curve line for depolymerization process

3.7.5 Procedure treatment of product from microwave

This section is the most important section in the practical part and is divided into two parts.

3.7.5.1 Neutralizing solutions

When the set temperature is reached, and after the polyethylene terephthalate depolymerization time is completed inside the reactor, the containers begin to cool automatically, and after making sure that they are cooled, the Teflon tubes are taken out from inside the containers with extreme caution, and these tubes are emptied into a glass beaker see Figure (3.26). The Teflon tubes are washed with distilled water several times and added to the rest of the solution in the glass beaker. Then, the solution was neutralized with hydrochloric acid (10% vol./vol.) by adding it using a graduated burette (with a 50% phenolphthalein solution as an indicator). See Figure (3.27).

Figure 3.26 Solution befor adding indicator

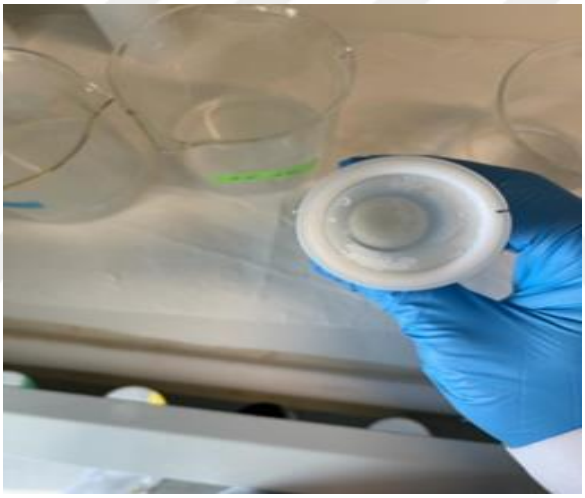


Figure 3.27 Solution from reacter

When the 3 or 4 dropes from the indicator which (Phenolphthalein solution50%vol./vol.) is added to the solution, the color of the solution changes. to violet color see Figure (3.28), and we add(HCL10% vol./vol.)from purait and by drop by drop its almost take 14 ml from HCL, when the neutralization point is reached the color disappears i.e. the solution is close to (PH = 7) the solution contains EG, Disodium terephthalate and TiO_2 dissolved plus residual PET if there is a residual see Figure (3.29). Thus, the solutions were prepared for the filtration process.

Figure 3.28 Solution after adding indicator

Figure 3.29 Solution after neutralization

3.7.6 Solutions filtration

Before performing the filtration process, the filter papers are prepared, numbered and weighed accurately, and the weights are written in order to calculate the amount of PET remaining after the filtration processes see Figure (3.30). After the filtration procedure, we take the filter papers by carefully lifting them from the filter funnel and placing them in plastic containers and entering them into a drying oven for 24 hours. See Figures (3.31,3.32,3.33)After this period of time, the filter papers are weighed again after making sure that the moisture is gone from these papers. Thus, the remaining weight of

PET can be known by the following equation: PET remains = Wt. empty filter paper - Wt. filter paper after drying.

Figure 3.30 Filter papers prepired for dring

Figure 3.31 Solution of filtration

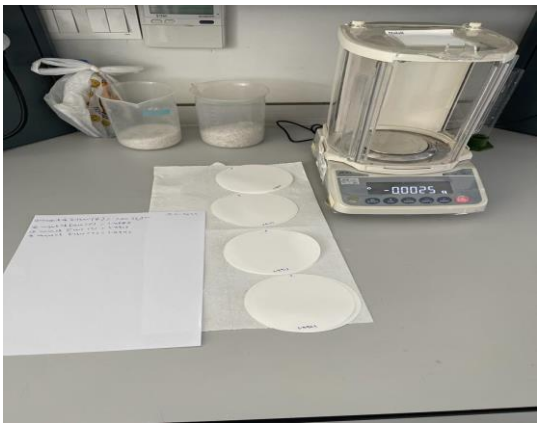


Figure 3.32 Weighting filter papers

Figure 3.33 Dring filter papers

The solution was filtered using a Buechner filter with a double layer of filter paper to separate the unreacted PET from the rest of the solution see Figure (3.31).

TPA is precipitated by the addition of concentrated hydrochloric acid HCL, where PH = 2 is reached see Figures (3.34,3.35).

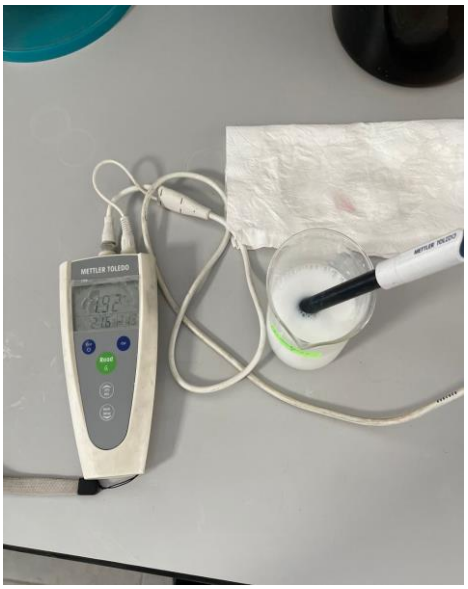


Figure 3.34 Precipitates TPA at PH=2

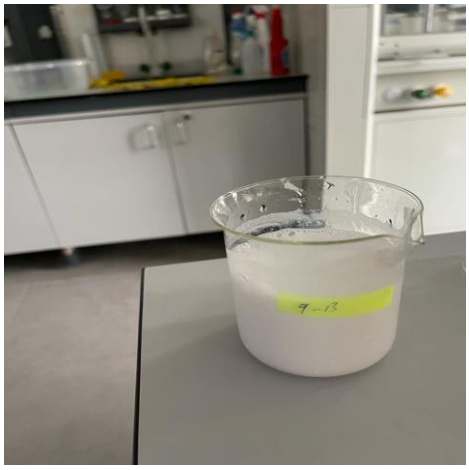


Figure 3.35 TPA precipitated

TPA appears as a layer of white crystals. Then, the TPA crystals are collected through filtration, where they are in the form of a white film on the surface of the filter paper. See Figure (3.36).

Figure 3.36 Filtaring TPA solution

Pure TPA results from the reaction between hydrochloric acid (HCl) and disodium terephthalate which is a double replacement reaction that produces terephthalic acid and sodium chloride as products. The balanced chemical equation for this reaction is:

$$2Na_2C_8H_4O_4\ (s) + 4\ HCl\ (aq.) \rightarrow 2\ C_8H_6O4\ (s) + 4\ NaCl\ (aq.) + H_2O\ (l)$$

In this reaction, disodium terephthalate ($Na_2C_8H_4O_4$) reacts with hydrochloric acid (HCl) to form terephthalic acid ($C_8H_6O_4$), sodium chloride (NaCl), and water (H_2O). The reaction begins by exchanging the sodium ions in disodium terephthalate with hydrogen ions from hydrochloric acid to form terephthalic acid, which precipitates out of solution as a white solid powder. After separating the terephthalate layer by filtration again, a layer is formed on the surface of the filter paper. This layer is inserted into the oven for 24 hours at a temperature of 70 degrees Celsius for drying. after that samples are collected in bags and prepared for the diagnostic and analysis process. See Figure (3.37).

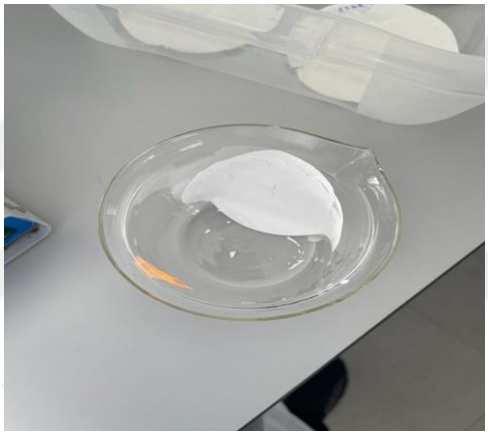


Figure 3.37 Drying TPA

3.8 Calculations of PET Depolymerization

Balance was used to determine the Remaining PET amount and percent depolymerization of PET, which was defined as:

Remaining PET amount = $W_{(in)}PET - W_{(f)}PET$

PET Depolymerization(%) = $(W_{(in)}PET - W_{(f)}PET / W_{(in)}PET) *100$

Where $W_{(in)}PET$ is the initial weight of PET and $W_{(f)}PET$ is the weight of PET that remains after the reaction was ended.

4. RESULTS AND DISCUSSION

In this chapter, we review all the results of the experiments of the process of depolymerization of PET using (the Taguchi design)Method and ANOVA, we use (the Taguchi design) and(regression equation), for find the optimum conditions for depolymerization and also explain the effects of conditions such as temperature, time, catalyst, and the effect of the alkaline base (NaOH) on the depolymerization and remaining PET.

4.1 Remaining PET Measurement

Table 4.1, displays the results of the 36 experimental runs performed using the Taguchi design method. The Taguchi design approach is a popular experimental design model for three-level and four-factor trials (L9). The precision of the observations in the remaining runs is important to the model's trustworthiness in these configurations. This study performed the least squares regression ANOVA using Design Expert Software Minitab.

Using the fitted equation obtained from the regression analysis while holding one of the independent variables constant, the statistical software program was used to generate the model equation (regression equation), interaction effects of the four independent variables (Temperature, NaOH concentration, catalyst TiO_2 amount, and time of reaction) on the corresponding quality of the remaining PET.

After the reactions remaining PET amounts were measured and listed in Table 4.1

Table 4.1 Reaction conditions and remaining PET amounts

NO. runs	Reaction temperature (°C)	Reaction time (min)	Sodium Hydroxide concentration (%)	Catalyst amount (g)	Remaining PET amount (g)
1	165	10	4	0,01	1,3340
2	165	20	8	0,02	0,5222
3	165	30	12	0,03	0,1233
4	180	10	8	0,03	0,0097
5	180	20	12	0,01	0,0040
6	180	30	4	0,02	0,1101
7	195	10	12	0,02	0,0024
8	195	20	4	0,03	0,0055
9	195	30	8	0,01	0,0020
10	165	10	4	0,01	1,3030
11	165	20	8	0,02	0,4488
12	165	30	12	0,03	0,1184
13	180	10	8	0,03	0,0420
14	180	20	12	0,01	0,0021
15	180	30	4	0,02	0,1856
16	195	10	12	0,02	0,0012
17	195	20	4	0,03	0,0665
18	195	30	8	0,01	0,0013
19	165	10	4	0,01	1,3540
20	165	20	8	0,02	0,4883
21	165	30	12	0,03	0,1133
22	180	10	8	0,03	0,0083
23	180	20	12	0,01	0,0060
24	180	30	4	0,02	0,0688
25	195	10	12	0,02	0,0063
26	195	20	4	0,03	0,0388
27	195	30	8	0,01	0,0031
28	165	10	4	0,01	1,2370
29	165	20	8	0,02	0,5358
30	165	30	12	0,03	0,1607
31	180	10	8	0,03	0,0239
32	180	20	12	0,01	0,0030
33	180	30	4	0,02	0,1420
34	195	10	12	0,02	0,0015
35	195	20	4	0,03	0,0625
36	195	30	8	0,01	0,0009

In the Table (4.1), provided, the experimental conditions and corresponding values of the response variables (remaining PET) are listed. The table also shows the different levels of each factor that were used in the experiment. For example, the temperature was varied at three levels: (165, 180, and 195)°C. We have performed regression

analysis to find a linear equation (model) between reaction parameters and findings (remaining PET) Regression was found to be statistically significant and the regression model successfully predicted the remaining PET amount.

It is important to note that the amount of remaining PET is likely to be affected by factors other than those that were included in the experiment, such as the quality of the PET starting material , and the purity of the catalyst used. Therefore, it is important to consider these factors when interpreting the results of the experiment and drawing conclusions about the optimal reaction conditions.

4.2 Regression Analysis

Regression analysis is a statistical technique for modeling the connection between one or more independent variables and a dependent variable. In our study (Remaining PET), the dependent variable is the outcome or response variable that is predicted or explained, whereas the independent variable is the predictor variable that is utilized to explain the variation in the dependent variable.

The primary purpose of regression analysis is to create a mathematical equation or model that can predict the value of the dependent variable based on the independent variables' values. Fitting a line or curve to a set of data points to estimate the model, where the line or curve indicates the relationship between the independent and dependent variables.

Regression analysis is classified into two types: linear regression and nonlinear (Quadratic) regression. When the relationship between the independent and dependent variables is linear, linear regression is employed, but nonlinear regression is used when the relationship is more complex and cannot be represented by a straight line.

Analysis of regression. It is frequently used to analyze and forecast trends, forecast future occurrences, and calculate the impact of changes in one or more variables on the dependent variable.

4.2.1 Regression equation

The regression equation is a mathematical formula that describes the relationship between the response variable (in this case, the amount of remaining PET) and the predictor variables (temperature, time, concentration, and catalyst amount). See Table (4.2).

Table 4.2 Coefficaint for linear regrssion equation

Term	Coef	SE Coef	T-Value	P-Value	VIF
Constant	5,18900	0,40800	12,71	0,000	
Temperature	-0,02096	0,00218	-9,64	0,000	1,00
Time	-0,01789	0,00326	-5,48	0,000	1,00
Concentratıon	-0,05589	0,00816	-6,85	0,000	1,00
Catalyst Amount	-18,66000	3,26000	-5,72	0,000	1,00

The coefficients of the regression equation are listed in the first row (Coef) of the table. The constant term coefficient is 5.189, which indicates the estimated quantity of leftover PET when all predictor variables are zero. The coefficients for the remaining predictor variables (temperature, time, concentration, and catalyst quantity) represent the change in expected remaining PET associated with a one-unit increase in each variable while maintaining all other variables constant.

The standard error of the regression coefficient estimate is represented by (SE Coef). The standard error is a measure of the uncertainty or variability in the coefficient estimate. A lower standard error means that the estimate is more precise.

The P-value is the computed likelihood of a (false positive) or Type-1 error. The p-value for an effective factor in a%95 confidence interval should be less than 5% (0,050), and the P-value for an effective factor in a%99 confidence interval should be

less than 1% (0,010). Because all of (p-Values) are less than 1/1000, we can choose a confidence interval of %99, %99.5, or even %99.9. The(P-Values) in the regression equation are about the terms in the regression.

The t-statistic (T-Value) is used to test the null hypothesis that the regression coefficient is equal to zero. The t-value is a measure of how far the estimated coefficient is from zero. A large t-value (along with a small p-value) implies that the estimated coefficient deviates significantly from zero.

The variance inflation factor (VIF) quantifies the amount by which the predicted coefficient variance is enhanced due to multicollinearity among the predictor variables. A VIF score larger than one suggests that the predictor variables are multicollinear in some way. Higher VIF values indicate higher degrees of multicollinearity, which can lead to instability in regression coefficient estimations and impair model precision.we do not need to report (because VIF=1 so there is no multicollinearity among variables/inputs/reaction parameters)

For example $Y = N + ax_1 + bx_2 + cx_3 + dx_4$ and p=0.000 for x_1=(Temperature),x_2=(TIME), X_3=(CONCETRATION),X_4=(CATALYST AMOUNT) so this term is effective on regression. P=0.000 for constant (N) so his term is effective on the regression. In this regression all of the terms are effective on regression model. Due to the Raising temperature value lovering the remaining PET (Because it has a negative sign and negative T value) and so on. Regression analysis alone is not enough, we need to calculate R^2 value. It should be as high as possible (like %99) preferably more than 80-85%in table 4-3 (model Summary) for (R^2).

REMANING PET = 5,189 – (0,02096*TEMPERATURE) – (0,01789*TIME) – (0,05589*CONCENTRATION) – (18,66*CATALYST AMOUNT)

4.2.2 Model summary

The Table (4.3), model Summary provides information about the quality of the regression model used to predict the remaining PET amount.

Table 4.3 Model Summary FOR (R2)

S	**R^2**	**R^2(adj)**	**R^2(pred)**
0,159840	86,73%	85,02%	81,93%

The (S) denotes the estimate's standard error, which is a measure of the average gap between the actual and anticipated values. The standard error in this example is 0.159840.

The (R^2) denotes the coefficient of determination, which measures the proportion of variation in the dependent variable (remaining PET amount) that can be explained by the independent variables (reaction temperature, reaction time, sodium hydroxide concentration, and catalyst amount). In this situation, the R^2 value is 0.8673, indicating that the independent variables in the model explain approximately 86.73% of the variation in the residual PET quantity.

The R^2(adj) reflects the adjusted R^2 value, which takes the number of independent variables in the model into consideration and changes the R^2 value accordingly. The modified R^2 value of 0.8502 indicates that the model's independent variables explain a considerable portion of the variation in the residual PET quantity.

The R^2(pred) provides the projected R-squared value, which measures the fraction of variation in a new dataset that the model can predict. The projected R^2 value of 0.8193 indicates that the model predicts the residual PET amount reasonably well in new datasets.Based on the values of the independent variables, the regression model fits the data well and may be used to forecast the remaining PET amount.

4.3 Analysis of Variance (ANOVA) Test

Equation of the remaining PET amount based on the effective parameters (temperature, time, sodium hydroxide concentration, and catalyst This table shows the results of an Analysis of Variance (ANOVA) for the regression amount).

Table 4.4 Analysis of Variance effective parameters

Source	DF	Adj SS	Adj MS	F-Value	P-Value
1-Regression	4	5,17619	1,29405	50,65	0,000
TEMPERATURE	1	2,37309	2,37309	92,88	0,000
TIME	1	0,76820	0,76820	30,07	0,000
CONCENTRATION	1	1,19957	1,19957	46,95	0,000
CATALYST AMOUNT	1	0,83533	0,83533	32,70	0,000
2- Error	31	0,79201	0,02555		
Lack-of-Fit	4	0,76778	0,19195	213,88	0,000
Pure Error	27	0,02423	0,00090		
Total	35	5,96820			

The Table (4.4) is divided into two main sections: Regression and Error: 1-The Regression section : The degree of variability described by the regression equation is shown. With an F-value of 50.65 and a p-value of 0.000, it suggests that the regression model is significant. This indicates that the regression model fits the data well and that the independent variables (temperature, time, concentration, and catalyst amount) are strong predictors of the remaining PET amount.

The table also displays how much each independent variable contributes to the model. For each variable, the Adjusted Sum of Squares (Adj SS), Adjusted Mean Square (Adj MS), F-value, and p-value are listed. Each independent variable's significance is measured by the F-value, with higher values indicating more relevance. The residual PET quantity is significantly affected by all four independent variables (p-value 0.01).

2- The Error section: displays the amount of variation that the regression model does not explain. The Lack-of-Fit metric measures how well the model fits the data, while the Pure Error metric measures the variability of the data around the regression line. With an F-value of 213.88 and a p-value of 0.000, the Lack-of-Fit is significant, indicating that the model might be improved by considering more variables or interactions..

Finally, the Total row displays the data's total variability, which is the sum of the regression and error variability.The influence factor, temperature, has the greatest value of (F). It is very clear that all of our factors are highly effective on the output (remaining PET) as it (F=92,88), which is the highest value for that we put the temperature as the most influencing factor for the depolymerization process, and then the base (NaOH) concentration comes at a degree of (45,95), and after them (the amount of catalyst and time) respectively by (32.70 and 30.07).

To show the effects between variables and remaining PET we use plots to show the influences of variables on depolymerization process.

4.3.1 Main effect plote from regression analysis

Main effect plots are used in regression analysis to visualize the relationship between each independent variable (or predictor variable) and the dependent variable (or response variable) while holding all other variables constant. In other words, they show the effect of changing one variable on the response, while keeping the other variables constant.

The main effect plot will display the values of the response variable on the y-axis and the values of the predictor variable on the x-axis. It will show a line or curve that represents the predicted values of the response variable at different levels of the predictor variable while holding all other variables constant.

The slope of the line or curve indicates the strength and direction of the relationship between the predictor and response variables. If the line or curve is horizontal, it suggests that the predictor variable does not affect the response variable. If it is sloping upward , it indicates a positive relationship, while a downward slope suggests a negative relationship.

By examining the main effect plot, you can gain insights into how changes in the predictor variable impact the response variable , and determine whether there is a significant relationship between the two.

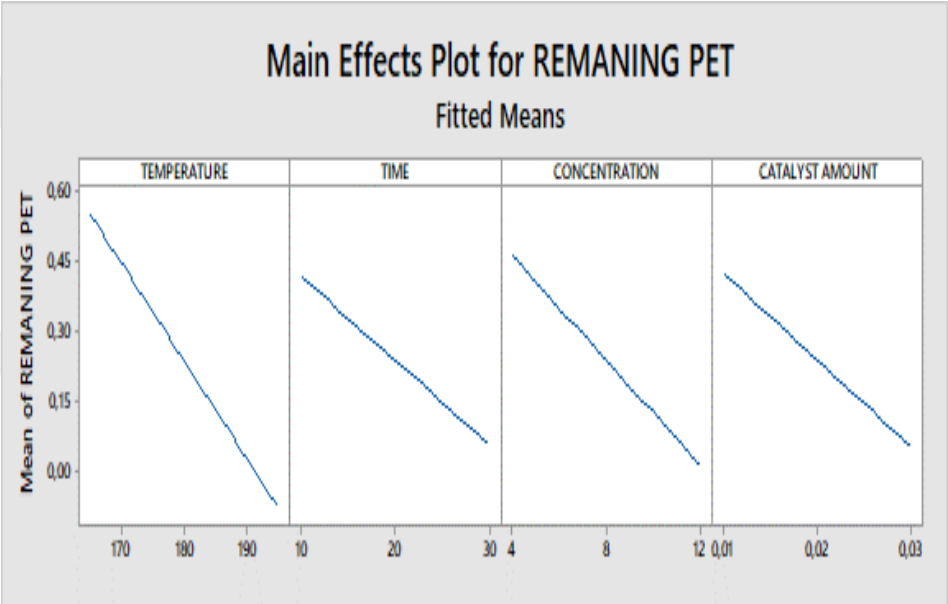


Figure 4.1 Main effect plots from linear regression

As we can see plots in Figure (4.1), it is a Linear model, where the amount of PET begins to decrease due to the effect of temperature, time, the catalyst and the concentration of the base, where the temperature acts as the first factor affecting the depolymerization, where it can be observed that the line following the temperature descends to zero compared to the remaining PET, and because we use the linear regression equation All fonts for effects will be linear.

4.3.2 Taguchi mthod (S/N) plotes

We begin the Taguchi approach by calculating signal/noise ratios. The signal-to-noise ratio (S/N) is a statistical measure used to evaluate the quality of a product or process.

The "signal" in this example refers to the desirable or crucial output or reaction of a process, whereas the "noise" refers to any other fluctuation or elements that may alter the output unfavorably. The Taguchi method's purpose is to maximize the S/N, which means maximizing the signal while minimizing the noise, to obtain ideal performance and quality. Different types of S/N measures can be used in the Taguchi method, depending on the nature of the process and the desired outcome.

Some common examples include: - Larger the better (LTB) S/N: When a higher production is sought (for example, in a manufacturing process where a higher yield is preferred), - Smaller the better (STB) S/N: When a smaller output is desirable (for example, in a process where a lower failure rate is preferable), - Nominal the best (NTB) S/N: When a specified goal value is sought (for example, in a process where a specific dimension or tolerance must be met).

The Taguchi approach helps determine the ideal settings that will yield the best results while minimizing the impact of noise elements by analyzing the S/N for different parameters and levels of a process. See Figure (4-2).To evaluate the influence of (tempruter, time, catalyst amount, concentration of alkalin solution), the signal-to-noise (S/N) ratio was used. The equation was used to calculate S/N ratios : $S/N= -10 *\log_{10} (\sum Y^2)/n$. Where (Y) is the factor level and (n) is the number of variables, based on the "smaller-the-better" approach.

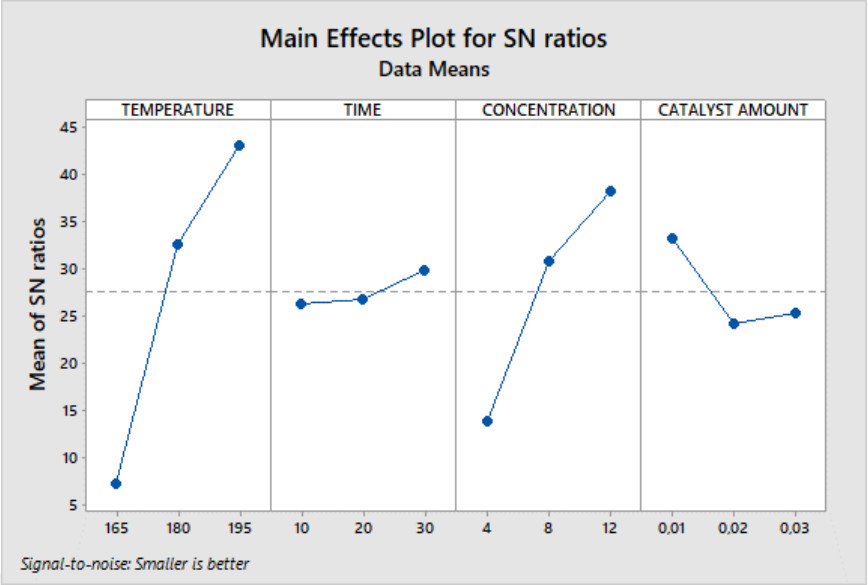


Figure 4.2 Main effects Plot for S/N ratios

In our case we want to minimise Remaining PET amount so we need to choose "Smaller is Better" approach. For more grasp we need to draw main Effects Plot for means.

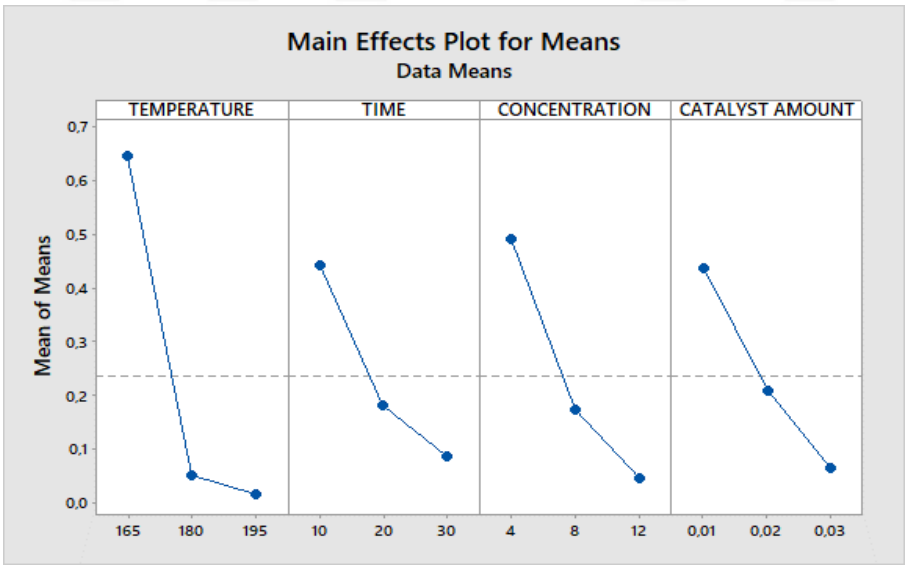


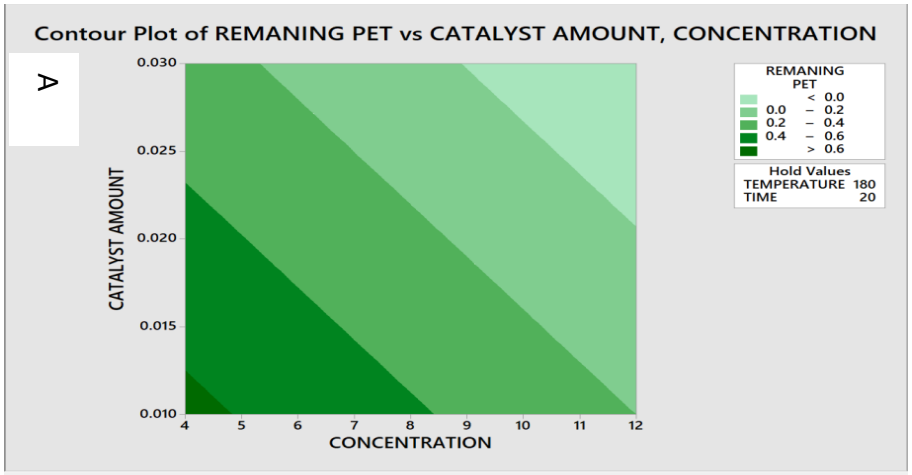
Figure 4.3 Main effects plot for means

From Figure (4.3) its clearly When you increase temperature remaining PET (y-axis) lowers. When you increase reaction time remaining PET (y-axis) lowers and when

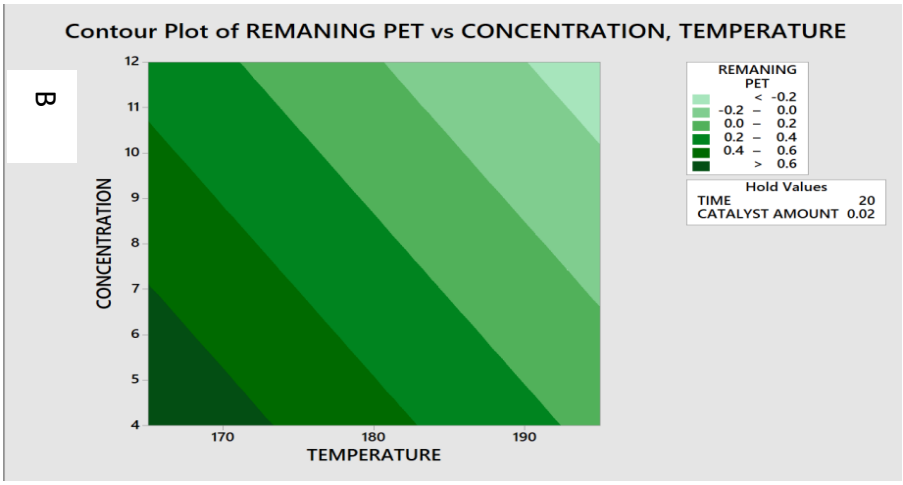
increase the NaOH concentraion the remaining PET lower at last the catalyst amout when we add more amount of catalyst the remining PET lowers.

4.3.3 Contour plots

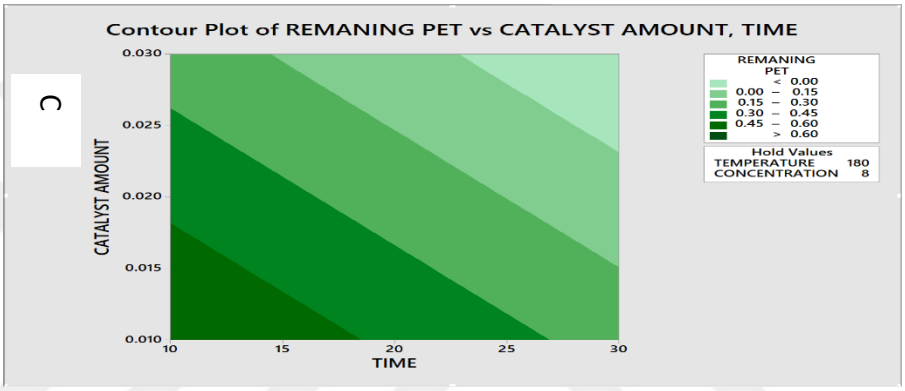
The contour diagrams in Figures (4.4), A, B, C, D, E, and F show two independent variables(two influences effect)and one response, which is the (remaining PET), when the third variable is constant, as the plots show the extent to which these the response. By looking at the graphs in Figures (4.4) A, B, C, D, E, and F we notice significantly the effect of temperature and concentration on depolymerization where the area of the darker region (less than 0.6) (concentration against heat). The value (F) where the value of F for temperature = 92.88 and the value for concentration F = 46.95 and thus the largest area of ideal points appears in this figure (Temperature *concentration) see Figure (4.4) B. We also note the convergence of the two Figures (4.4) DandF which is (Temperature*catalyst) with (time *Temperature) plot, because the value of (F) for time and quantity of catalyst is very close, reaching (30.07) for time and (32.70) for catalyst, and this gives us the same very close figures. In the two Figures (4.4) AandE(Catalyst *concentration) as well as (time * concentration), we notice that there is little space to find the ideal points, which are very similar due to the closeness of the F-value for time and Catalyst. In Figure (4.4) C(Time*catalyst) We notice the disappearance of the area less than 0.6 because the value of F is the lowest value between the two effects, and therefore we need to increase these two effects to reach the ideal points.



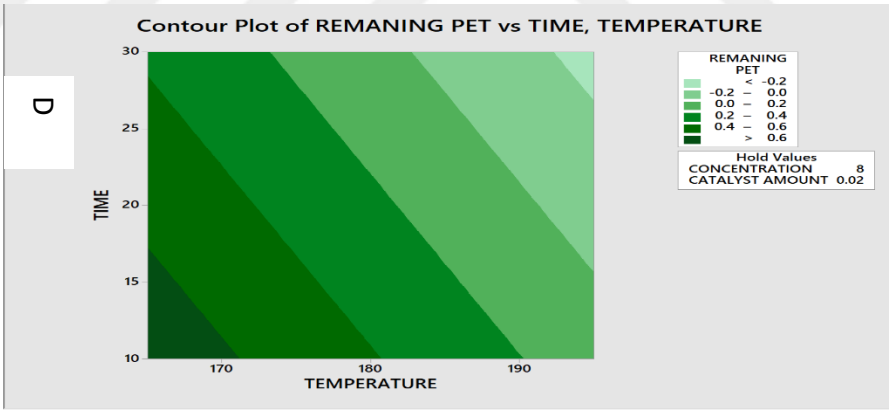
B


Contour Plot of REMANING PET vs CONCENTRATION, TEMPERATURE
CONCENTRATION
TEMPERATURE
REMANING PET
< -0.2
-0.2 – 0.0
0.0 – 0.2
0.2 – 0.4
0.4 – 0.6
> 0.6
Hold Values
TIME 20
CATALYST AMOUNT 0.02

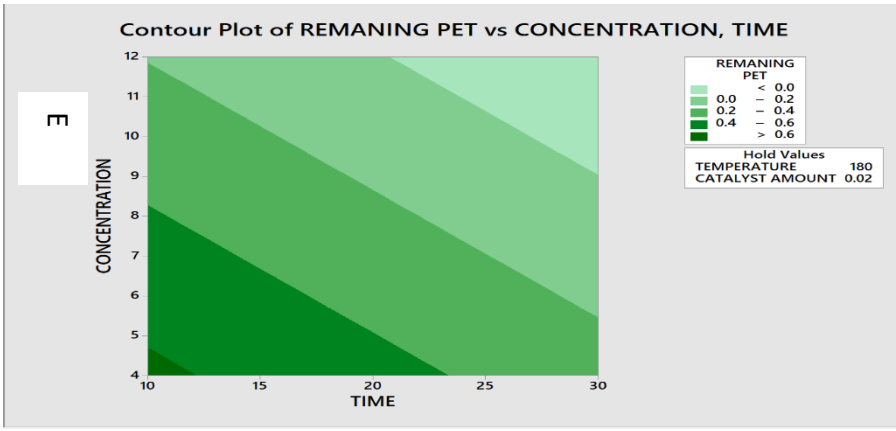
C


Contour Plot of REMANING PET vs CATALYST AMOUNT, TIME
CATALYST AMOUNT
TIME
REMANING PET
< 0.00
0.00 – 0.15
0.15 – 0.30
0.30 – 0.45
0.45 – 0.60
> 0.60
Hold Values
TEMPERATURE 180
CONCENTRATION 8

D


Contour Plot of REMANING PET vs TIME, TEMPERATURE
TIME
TEMPERATURE
REMANING PET
< -0.2
-0.2 – 0.0
0.0 – 0.2
0.2 – 0.4
0.4 – 0.6
> 0.6
Hold Values
CONCENTRATION 8
CATALYST AMOUNT 0.02

E


Contour Plot of REMANING PET vs CONCENTRATION, TIME
CONCENTRATION
TIME
REMANING PET
< 0.0
0.0 – 0.2
0.2 – 0.4
0.4 – 0.6
> 0.6
Hold Values
TEMPERATURE 180
CATALYST AMOUNT 0.02

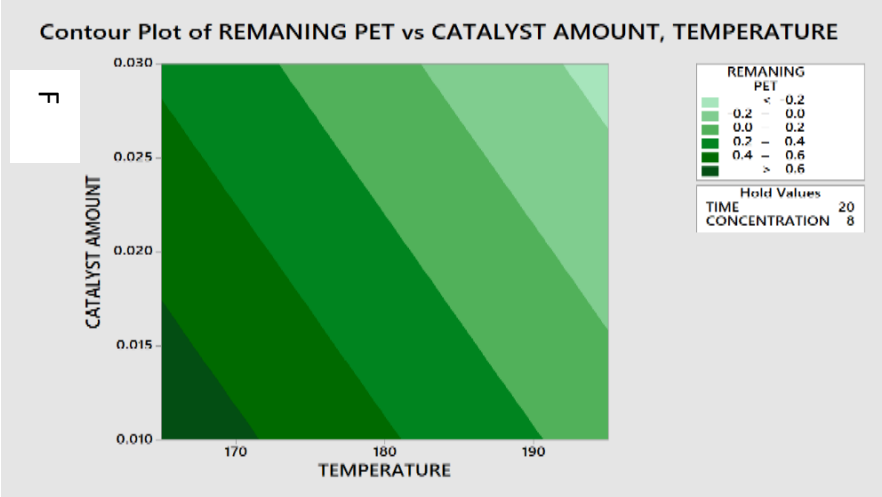


Figure 4.4 Contour plots

4.4 Factors Affecting Depolymerization

4.4.1 Partical size distribution effict

Thermoplastic polymers include polyethylene terephthalate (PET). Through a chemical process, PET can be broken down into its monomers. This process usually makes use of a catalyst as well as basic or acidic depolymerizing solutions.PET particle size is one of many variables that might influence PET depolymerization. When PET particles are reduced in size, their overall surface area increases in volume. The PET can be in contact with the depolymerization catalyst and the base solution more effectively thanks to the increased surface area, and even temperatures are uniform if all particles have the same surface area to volume ratio. Additionally, the depolymerization catalyst may have an easier time penetrating smaller particles, which may enable the catalyst to break down the polymer chains more effectively. Smaller particles have shorter diffusion lengths than larger ones, which makes it simpler for the depolymerization catalyst to enter the particles and interact with the PET polymer chains. The depolymerization process can be significantly impacted by the kind and concentration of the depolymerization catalyst, the reaction temperature and time, and the presence of impurities. Hence, by optimizing each of these characteristics, TiO_2 achieves effective depolymerization of PET; a house cut between the sizes of 2000 and 3000 µm was used

in our experiments. However, we do not know with certainty how close the percentage of these pieces is to the size of 2000μm or closer to the size of 3000 μm.

4.4.2 Temperature effict

To study the effect of temperature on the Depolymerization from PET under microwave irradiation, different sets of reactions were performed at different temperatures, namely, 165, 180, and 195ºC. was The catalyst used in these reactions Titanium dioxide, TiO_2, at concentrations of 0.1, 0.2, and 0.3 grams. The volume of solvent was 30 ml of concentrations of (4, 8, and 12) %. The reaction temperatures investigated were 165 to 195 °C.

The results (see Table 4.1) indicate that the remaining PET decreases with increasing temperature. At a temperature of 165 ºC, taking the best-suggested conditions for the rest of the effects, the best result for the remaining PET is 0.1133 grams. The conversion of PET increased with the increase in temperature. The rise in temperature at 180, will reduce the amount of remaining PET, as the best result is 0.0021 grams, and with an increase in temperature at 195 ºC, PET will decrease significantly, reaching 0.0009 grams, which is an excellent result for the depolymerization process of these values as well. In figure (4-2) and Figure (4-3), we note that the temperature is the biggest influencer, as the response gradually decreases with a decrease in temperature. We also notice a large difference in the response between the temperatures 180 ºC to 165ºC, as it approaches zero at a temperature of 190 ºC, while there is a very small difference compared to the time in which degrees The degree of time is between (10-20) minutes, while the largest difference occurs in the response in concentration at a concentration of (4-8)% wt/vol.

4.4.3 Time effict

The effect of reaction time on the complete conversion of PET under microwave irradiation was investigated in the time range of 10, 20, and 30 minutes with several values of time, temperature, and catalyst variables see Figure (4.3) (It can be easily

observed that the increase in reaction time increases the depolymerization and conversion of PET into TPA, as the increase in the time factor gives more opportunity for heat as well as the rest of the variables to work more to break the bonds between the monomer molecules and thus contribute more to the removal of polymerization

As the relationship is direct between time and depolymerization, here we can conclude that time significantly affects the conversion process to TPA The time is approximately between (10 -20) minutes. Its response is equal, as noted in Figure (4.2), compared to the rest of the effects, where a slight change appears in the response. After that, the response increases upon reaching 30 minutes.

4.4.4 Concentration NaOH effict

The effect of alkalinity is another parameter being studied. Concentrate the solution (NaOH) on the TPA yield. The rate of hydrolysis PET appears to increase with NaOH concentration. However, while using intense alkaline solutions, one must strike a balance. Because of the additional expense and the increased volume of NaOH, It was created by recovering the biggest monomer. Three concentrations were employed in different situations for additional impacts, but as shown in Figure (4.2), the residual PET diminishes as the concentration of NaOH increases, where three concentrations were tested namely 4, 8, and 12, %wt/vol. From Figure (4.3) notes the largest change in the response between (4-8)%, where there is a big difference between these two concentrations in terms of response compared to time and also the amount of the catalyst when reaching a concentration of 12%. This is considered the largest response to concentration.

4.4.5 Catalyst (TiO_2) effict

The use TiO2 of as a catalyst has been proposed to facilitate PET's hydrolysis alkaline conditions. At concentrations (0.1, 0.02, and 0.03) gram after the completion of depolymerization The effect of using the catalyst on the amount of residual PET was shown During alkaline hydrolysis of PET under microwave The irradiation was also

investigated here. The results were in favor of the work. The results obtained using the highest motivating factor are superior to the other results To which the lesser amount of catalyst is added, the catalyst helps the reaction by helping the base solution to break the bonds between the monomers and convert them into smaller chains. see Figure (4.3)

By looking at Figure (4.2), we notice that there is a difference in the response between (0.01-0.02)g, but the difference in response between (0.02-0.03)g is very small compared to temperature as well as concentration, but it is similar to the response to time between (20-30)minutes Accurate and this is why it is logical to say that the biggest influence is the temperature and concentration and this has been proven statistically.

4.5 Optimization Method

Establishing factor values that limit response variability around a desirable target value (or target function in the case of a dynamic response experiment) is frequently the goal of a robust parameter design. This is accomplished via Taguchi methods using a two-step optimization strategy. The first step emphasizes reducing unpredictability, and the second step emphasizes hitting the target. Start by setting all variables that significantly affect the signal-to-noise ratio to their highest value. Adjust the level of one or more parameters that significantly affect the mean (or slope) but not the signal-to-noise to get the response where you want it. The standard deviation can also be reduced first, and then a variable that affects the mean but not the standard deviation is changed.

We know the relationship between reaction parameters and output since we have our major effects charts. We want to achieve very low, if not zero, output. Simply choose the charts with the highest values for the S/N primary effect. (30 minutes at 195°C, a 12 wt/vol. concentration, and a 0.03g catalyst) When utilizing main effect plots for means, you'll receive the same parameter levels. These two Figures (4.2,4-3) are mirror images of each other because we are using a smaller, better approach. Let’s use these values in the regression equation.

4.5.1 Prediction for remaining PET

By using linear regression equation and putting data (195^{o}C, 30 minutes, 12% concentration NaOH, 0.03g catalyst) into the regression equation yields -0,666368 grams of residual PET. See Table (4.5) Because this is a linear equation, a very minimal error is expected. This is the first of our optimum points. We did not perform a reaction at 195°C for 30 minutes with a %12 concentration and a 0.03g catalyst, because we are certain that these conditions will result in no residual PET.

Regression Equation for first optimum points:

REMANING PET = 5,189 - 0,02096 TEMPERATURE - 0,01789 TIME - 0,05589 CONCENTRATION- 18,66 CATALYST AMOUNT

Table 4.5 Variable setting for regression equation

Variable	Setting
Temperature	195^{o}C
Time	30 minutes
Concentration	12% NaOH wt/vol.
Catalyst Amount	0,03% wt/wt

The computer will give you this data

Fit	SE Fit	95% CI	95% PI
-0,666368	0,0704827	(-0,810119; -0,522618)	(-1,02265; -0,310085)

The model's ability to fit the data is shown by the SE Fit (standard error of the fit), which is 0.0704827. The predicted value's 95% confidence interval (CI) is (-0.810119; -0.522618), and this indicates that we are 95% certain that the true value of the remaining PET is within this range. The anticipated value's 95% prediction interval (PI), which is (-1.02265; -0.310085), indicates that we are 95% certain that a subsequent observation of the remaining PET will fall within this range.

4.5.2 Final optimum parameter level selection

There are numerous optimum positions to be identified. As a result, we should choose one of them. By using desired constraints in our experimental design, let us find an optimum point.

Constraints:

1. It should be lower than 30 minutes
2. It should be lower than %12 concentration

We put this constraint Because we need to fast reaction and use a low NaOH concentration. because it is not cheap. By finding an optimization response for PET remaining, taking into account the proposed limitations and targeting (0,000)gm of remaining PET, with a concentration of less than 12% and a minimum time of fewer than 30 minutes, we find the optimal degree for us.

4.5.3 Response optimization for remaning PET

By using our regression equation and by choosing the time of 20 mint and a concentration of 4% with computer 195 ^{o}C we find our catalyst amount between(0.01 to 0.03) g of TiO_2 the computer will give the weight of the catalyst and fit weight of the remaining PET as shown below.

Parameters:

Response	Goal	LowerTarget	Upper	Weight	Importance
Remaning PET	Target	-0,0000	1,354	1 g	1

We put the Variable Ranges:

Variable	Values
Temperature	195 ^{o}C
Time	20 minuts
Concentration	(4; 12) wt/vol.
Catalyst Amount	(0,01; 0,03) g

By using the values of the variable we found the remaining PET

Solution:

Temperature	Tıme	Concentratıon	Catalyst Amount	Remanıng Pet Fit
195^{O}C	20mint	4%	0,0278382g	0,0000040 g

Foundin of Multiple Response Prediction:

Variable	Setting
Temperature	195ºC
Time	20 minuts
Concentration	4% Wt/vol.
Catalyst Amount	0,0278382 g

Response	Fit	SE Fit	95% CI	95% PI
Remaning Pet	0,0000	0,0591	(-0,1205; 0,1205)	(-0,3476; 0,3476)

The multiple response prediction are shown in the table as follows:

Fit: At the independent variable's provided settings, the projected value of REMAINING PET is 0.0000. This indicates that, on average, the anticipated value of REMAINING PET at the given settings is 0.0000 units.

SE Fit: The predicted value of REMAINING PET has a standard error of 0.0591. This number shows the amount of random error brought on by sampling variability in the expected value of REMAINING PET.

95% CI: The anticipated value of REMAINING PET has a 95% confidence interval of (-0.1205, 0.1205). This indicates that, at the specified circumstances, we are 95% confident that the true value of REMAINING PET falls within this range.

95% PI: The expected value of REMAINING PET has a 95% prediction interval of (-0.3476, 0.3476). This indicates that we have a 95% certainty that a new observation of REMAINING PET made under the given conditions will fall within this range. By

using regression equation and take temperature 195^{0}C ,time 20 mint, concentration 4% and amount of catalyst 0.0278382 gm we predicted 0.0000040 gm of remaning PET.

Temperature	Time	Concentration	Catalyst Amount	Remining PET Fit
195^{0}C	20mint	4% Wt/vol.	0,0278382	0,0000040

These conditions 195^{o}C, 20 minutes, 4 % NaOH and 0.03grams catalyst are same conditions with experiment 8.in Table (4.1). Predicted of remaining PET is (0,0000040). There is a very very small variation between experimental results and predicted ones which is normal.

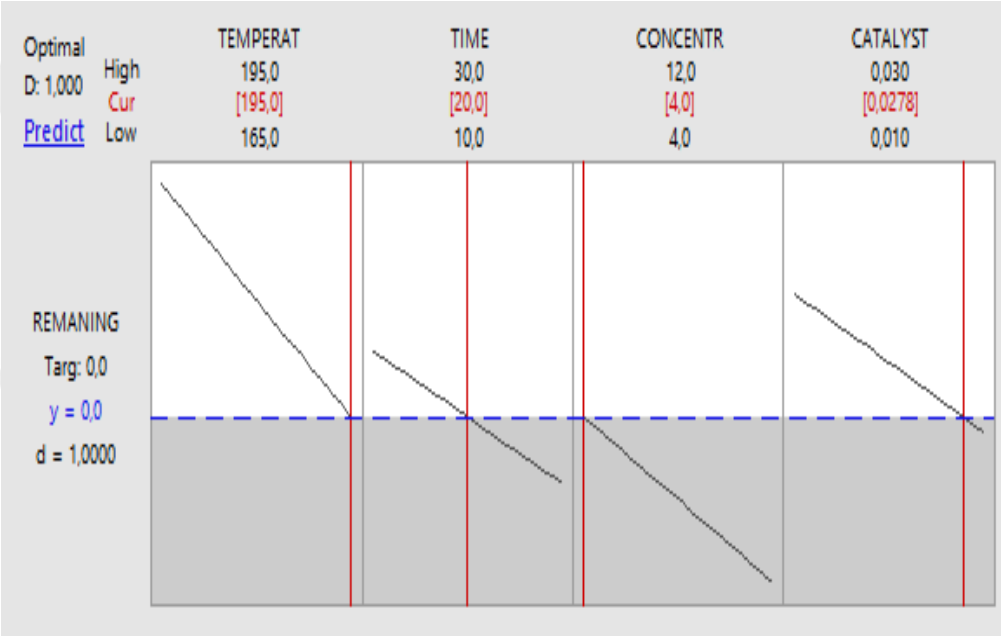


Figure 4.5 Optimization plots

The red line in the optimization plots see Figure (4.5) represents the average response value for the optimal combination of factor levels. This is the target value that you want to achieve. The blue line in the optimization plot represents the response values for each combination of factor levels tested in the experiment. This line helps you see how the response varies as the factor levels change. Ideally, you want the blue line to be as flat and close to the red line as possible, which indicates that the response is relatively insensitive to changes in the factor levels. The gray line in the optimization plot represents the signal-to-noise (S/N) ratio, which measures the response quality. In

Taguchi's design, the goal is to maximize the S/N ratio, which means minimizing the effects of noise (i.e., sources of variability that are not controlled by the factors). The Optimization plot is very good. All gray lines match with red lines. With this optimum point we have reached: 0 grams remaining PET with a low NaOH concentration in a relatively short time.

4.6 Microscop Photo Analysis

Using a high-resolution microscope, as in Figures (4.6) (a, b, c, d), we observe the external shape of the TPA at (2, 5, 10, and 20) micrometers, where we notice the presence of tubular shapes as well as cracks on the outer surface of the TPA.

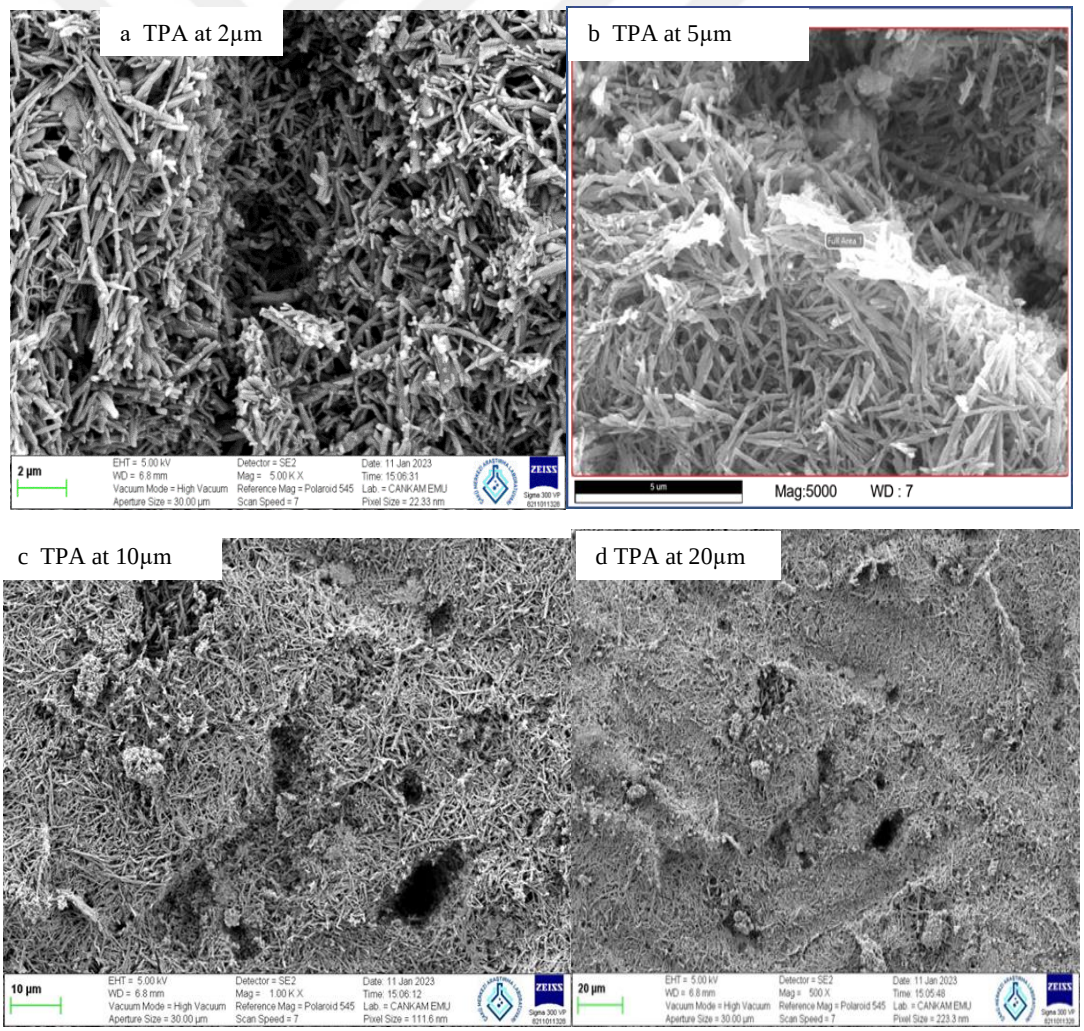


Figure 4.6 TPA

4.7 1HNMR Analysis

The structure and purity of the main product were confirmed by 1H-NMR spectrum as shown in Figure (4.7). The characteristic peaks of the isolated product and the commercially available standard were determined by 1H-NMR as follows: In the H-NMR spectrum Figure (4.7) and the structure of TPA shown in Figure (4.8), the signal at the chemical shift (δ) of 8.00 ppm shows the presence of four aromatic protons on the benzene ring. It was observed that the acid protons of the carboxyl group were at δ of 13.26. The two protons of group CH2 are observed at δ of 3.04. A signal at 2.47 was due to the solvent dimethyl sulfoxide-d_6 (Deuterated DMSO) and the humidity appeared at (3.36).

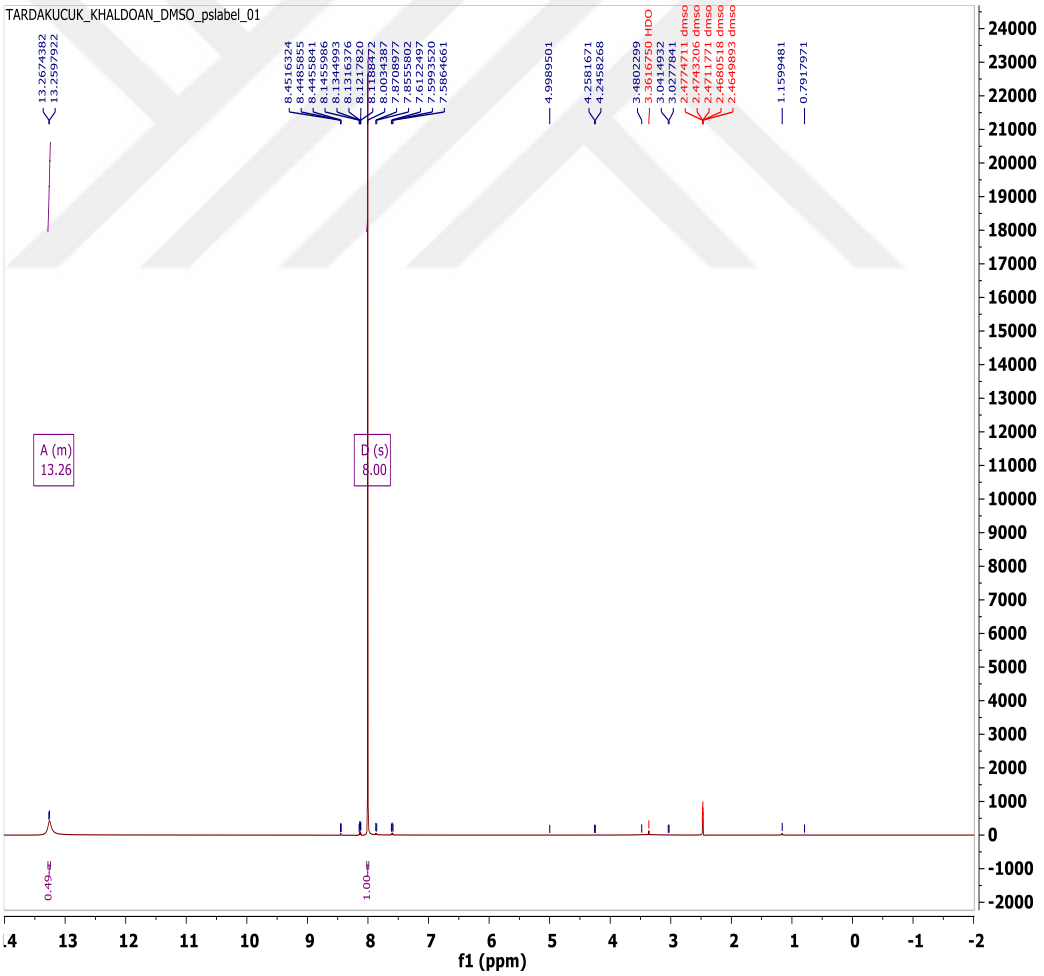


Figure 4.7 Representative 1 H NMR spectra of TPA product obtained from optimiztion reaction conditions during microwave alkalin hydrolysis process

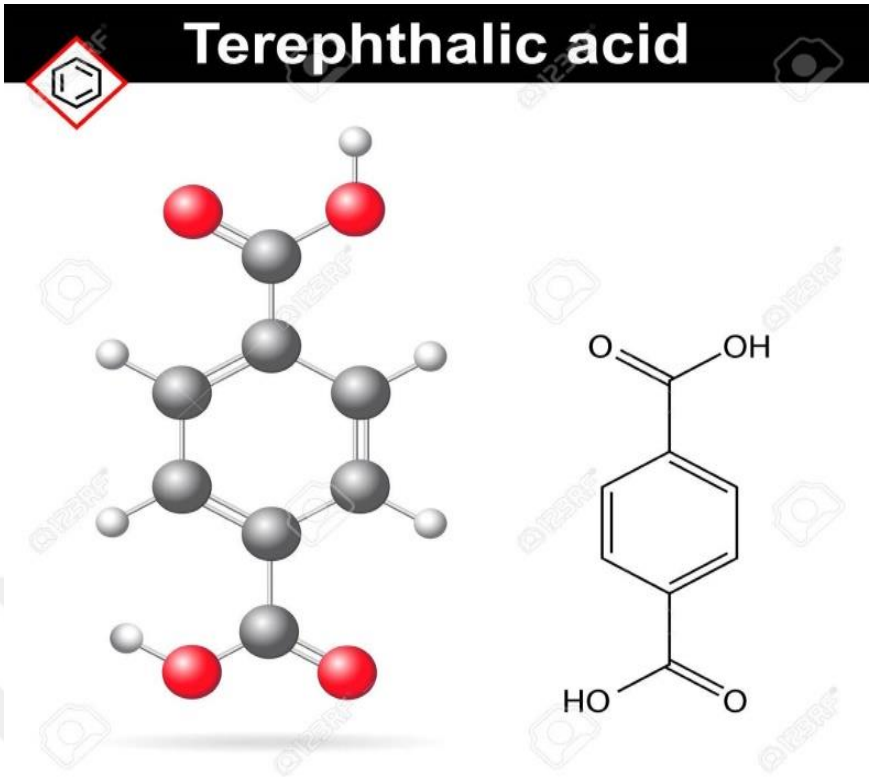


Figure 4.8 Chemical structure of TPA (Information 2021)

4.8 FTIR Analysis

FTIR spectroscopy was used to determine the distinctive chemical bonds in TPA, as shown in Figures (4.9 ,4.10). We note that the results match perfectly for the nine samples examined, while through Figure (4.11), the obtained organic aggregates were interpreted and explained as follows: The sharp band that appears at 3063 cm^{-1} is due to C-H aromatic expansion. The broad 3500 cm^{-1} band is due to the carboxylic acid (O-H) stretching vibration. The band at 1675.7 cm^{-1} is associated with (C=O) stretching vibration; the band observed at 1574 cm11280 cm^{-1} corresponds to the (C-C) aromatic ring vibration. The band is observed at 1423 cm^{-1} for C-H bending vibration. The band at 2819 cm^{-1} corresponds to aliphatic (CH). See Figures (4.11) Also, we can see more FTIR figures in Appendix 1.

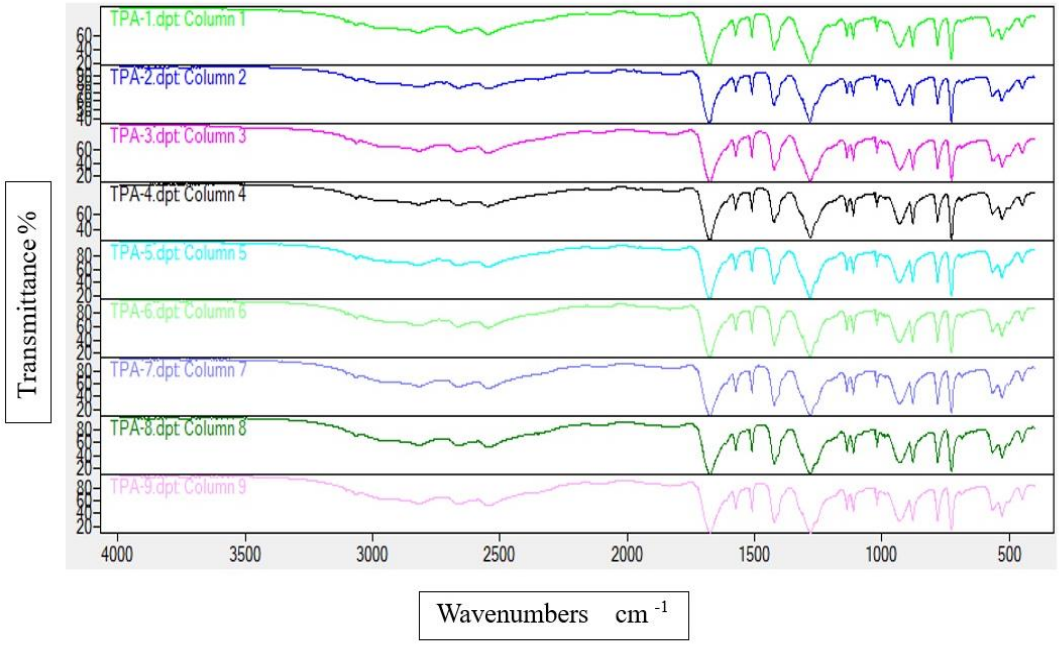


Figure 4.9 FTIR spectroscopy separated samples chart

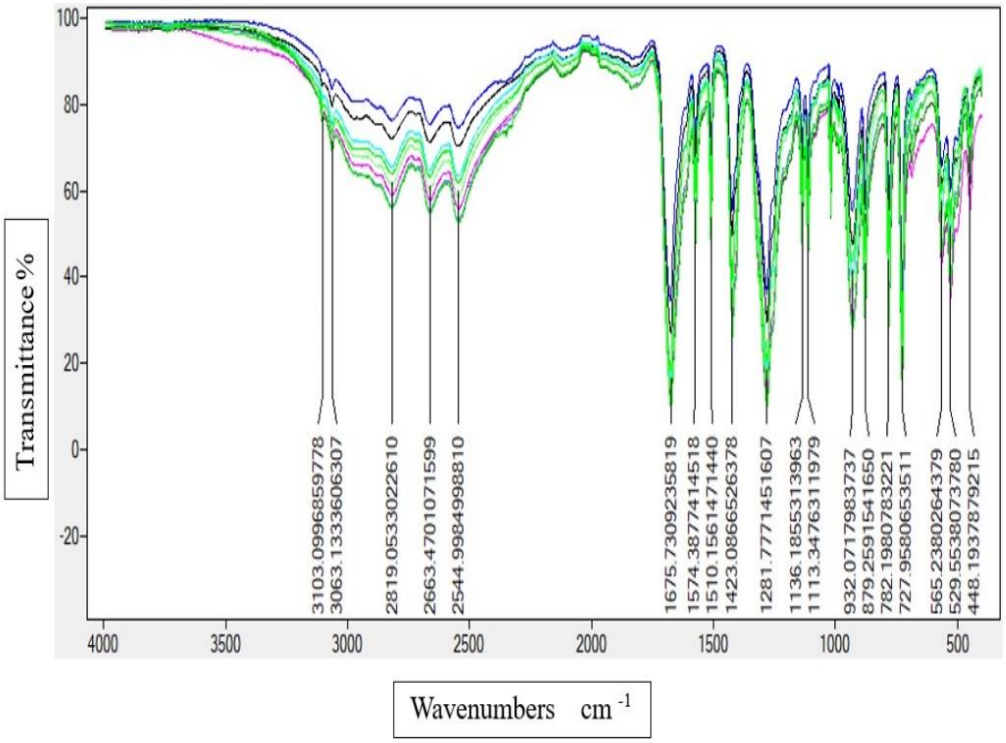


Figure 4.10 FTIR spectroscopy Over ALL samples chart

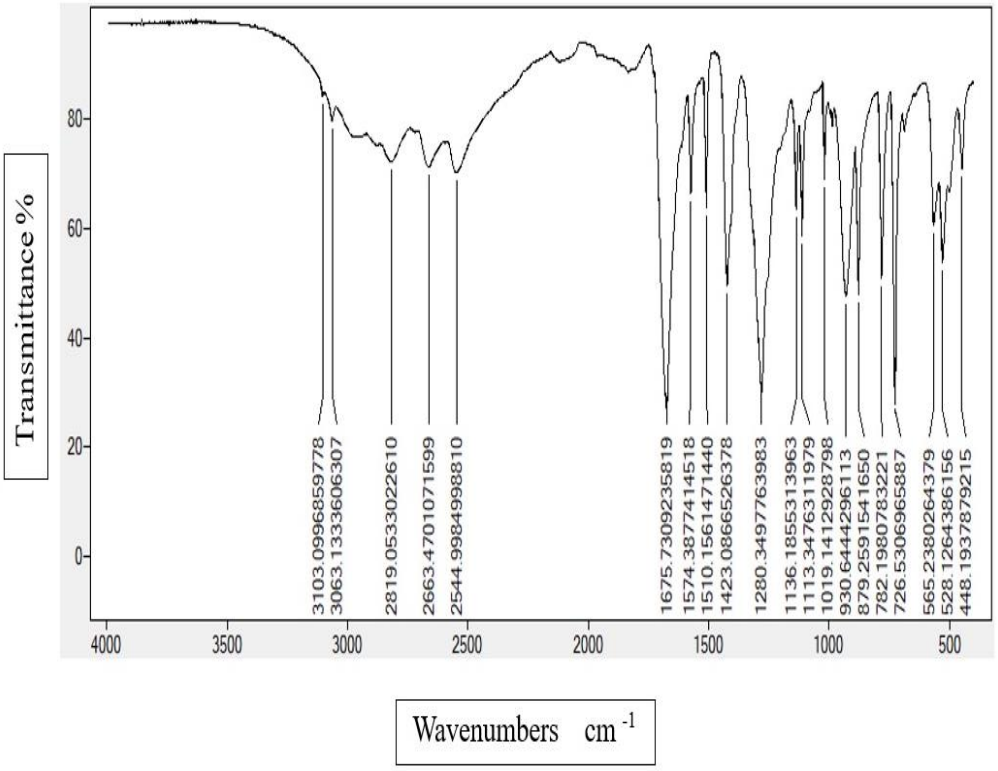


Figure 4.11 FTIR spectroscopy sample chart

5. CONCLUSIONS AND RECOMMENDATION

5.1 Conclusion

In this study, TPA was obtained by depolymerization of PET, which is considered one of the plastic wastes that greatly affect the environment, as well as reducing the economic waste of the plastic raw material and reducing the conversion or disposal operations that are not economically feasible for PET, as it also needs additional economic costs. A depolymerization process is performed in this study by changing four factors, namely temperature, time, NaOH concentration, and the catalyst, which is TiO_2, where a linear regression equation was reached through which logical expectations can be reached for PET depolymerization, and ideal points were found according to the restrictions set in Chapter 4 Among the results that have been achieved, it is logical to say that the goals previously mentioned in the introduction chapter have been achieved, as the Taguchi design was used to design experiments and analyze the experiments statistically, and we obtained a value ($P < 0001$) for all factors. as well as by drawing the contour diagram to link two influential factors to know the response of the outputs, which is the remaining PET, where ANOVA showed the effects of all variables on the outputs and predicted the responses. Many ideal points were obtained in our experiments, but using the imposed restrictions, results were obtained, which are 195^0C times 20 minutes. The concentration of 4% of the alkaline solution and the amount of catalyst were 0.027838 grams. The remaining PET was diagnosed and characterized by a microscope before and after depolymerization of PET, as well as the diagnosis of TPA by FTIR and 1HNMR, where the organic aggregates of TPA were clarified as they were identical to the chemical molecular structure of TPA. Nine samples of the product were measured, all of which were the same as each other, as shown in Chapter 4. It is worth mentioning that the use of a microwave reactor is considered an effective factor in the depolymerization process, as it contributed significantly to shortening the time and controlling variables such as the exact heat distribution for all parts of PET, as well as controlling and monitoring the depolymerization in general. The description of the depolymerization process is worth mentioning in this study. PET can be disposed of by

changing the four variables with a yield of up to 100% TPA to support the economic process, preserve the environment, and recover the economic value of PET.

5.2 Recommendation

To find an optimally effective path to yield TPA, an increase in actions must be taken, such as choosing more than one catalyst, using a mixture of catalysts, or using a mixture of alkalis that help break the bonds inside the PET. We also recommend increasing the surface area of PET because of its great effect on depolymerization and shortening of time, as well as the use of advanced reactors to control the depolymerization process, where it is possible to introduce other factors, including increasing the capacity of the reactor to reach ideal points for depolymerization.

In general, the aim of the study concerning depolymerization is to find the optimal and cheapest method for the PET recycling process. Therefore, it is necessary to simulate the process and estimate the costs of recycling PET waste with heavy weight using catalysts and different additives, compare the results of the costs relative to the final product, and understand whether the catalysts as well as the materials used competitively among themselves for chemical recycling An additional step can be a sustainability analysis of the recycling method for the optimal catalyst as well as for the materials used in the depolymerization process.

REFERENCES

Ahmed, T., Shahid, M., Azeem, F., Rasul, I., Shah, A. A., Noman, M., Hameed, A., Manzoor, N., Manzoor, I., and Muhammad, S. 2018. Biodegradation of plastics: current scenario and future prospects for environmental safety. Environmental Science and Pollution Research, 25(8): 7287–7298.

Al-Sabagh, A. M., Yehia, F. Z., Eshaq, G., Rabie, A. M., and ElMetwally, A. E. 2016. Greener routes for recycling of polyethylene terephthalate. Egyptian Journal of Petroleum, 25(1): 53–64.

Al-Salem, S. M., Lettieri, P., and Baeyens, J. 2010. The valorization of plastic solid waste (PSW) by primary to quaternary routes: From re-use to energy and chemicals. Progress in Energy and Combustion Science, 36(1): 103–129.

Alzuhairi, M. A. ., Khalil, B. I., and Hadi, R. S. 2017. Nano ZnO Catalyst for Chemical Recycling of Polyethylene terephthalate (PET). Engineering and Technology Journal, 35(8): 831–837.

Arias, J. J. R., and Thielemans, W. 2021. Instantaneous hydrolysis of PET bottles: An efficient pathway for the chemical recycling of condensation polymers. Green Chemistry, 23(24): 9945–9956.

Attallah, O. A., Janssens, A., Azeem, M., and Fournet, M. B. 2021. Fast, high monomer yield from post-consumer polyethylene terephthalate via combined microwave and deep eutectic solvent hydrolytic depolymerization. ACS Sustainable Chemistry and Engineering, 9(50): 17174–17185.

Awaja, F., and Pavel, D. 2005. Recycling of PET. European Polymer Journal, 41(7): 1453–1477.

Azeem, M., Fournet, M. B., and Attallah, O. A. 2022. Ultrafast 99% Polyethylene terephthalate depolymerization into value added monomers using sequential glycolysis-hydrolysis under microwave irradiation. Arabian Journal of Chemistry, 15(7): 10-13.

Barot, A. A., Panchal, T. M., Patel, A., and Patel, C. M. 2019. Polyester the workhorse of polymers: A review from synthesis to recycling. Archives of Applied Science Research, 11(2): 1-19.

Benyathiar, P., Kumar, P., Carpenter, G., Brace, J., and Mishra, D. K. 2022. Polyethylene terephthalate (PET) bottle-to-bottle recycling for the beverage industry: A Review. Polymers, 14(12): 23-36.

Blair, J., and Mataraarachchi, S. 2021. A review of landfills, waste and the nearly forgotten nexus with climate change. Environments, 8(8): 73-77.

Borrelle, S. B., Ringma, J., Law, K. L., Monnahan, C. C., Lebreton, L., McGivern, A., Murphy, E., Jambeck, J., Leonard, G. H., Hilleary, M. A., Eriksen, M., Possingham, H. P., and Rochman, C. M. 2020. Mitigate Plastic Pollution. Science, 15(18): 1515–1518.

Cao, F., Wang, L., Zheng, R., Guo, L., Chen, Y., and Qian, X. 2022. Research and progress of chemical depolymerization of waste PET and high-value application of its depolymerization products. RSC Advances, 12(49): 31564–31576.

Căta, A., Ştefănuţ, M. N., Ienaşcu, I. M. C., Tănasie, C., and Miclău, M. 2017. Alkaline Hydrolysis of Polyethylene Terephthalate Under Microwave Irradiation. Rev. Roum. Chim, 62(7): 531–538.

Čolnik, M., Knez, Ž., and Škerget, M. 2021. Sub-and supercritical water for chemical recycling of polyethylene terephthalate waste. Chemical Engineering Science, 23(3), 116-129.

Cong-hao, S., Xiang-ping, C., Qiang, Z., and Tao, Z. 2018. Recycling and depolymerization of waste polyethylene terephthalate bottles by alcohol alkali hydrolysis. Journal of Central South University, 25(3): 543–549.

Crippa, M., and Morico, B. 2019. PET depolymerization: A novel process for plastic waste chemical recycling. Studies in Surface Science and Catalysis, 179(2): 215–229.

Cywar, R. M., Rorrer, N. A., Hoyt, C. B., Beckham, G. T., and Chen, E. Y.-X. 2022. Bio-based polymers with performance-advantaged properties. Nature Reviews Materials, 7(2): 83–103.

Davidson, M. G., Furlong, R. A., and McManus, M. C. 2021. Developments in the life cycle assessment of chemical recycling of plastic waste – A review. Journal of Cleaner Production, 293(5): 126163.

Dos Santos, C. M. A., Gonçalves, A. C. R., Cintra, A. C., da Silva, L. A., Rossi, A., Oliveira, H. P., and Alves, V. A. 2018. Process of chemistry recycling of PET in

alkaline medium: Effect of concentration of hydroxide ion, color of PET and reaction time. Revista Materia, 23(4).56-66.

Dudyński, M., Van Dyk, J. C., Kwiatkowski, K., and Sosnowska, M. 2015. Biomass gasification: Influence of torrefaction on syngas production and tar formation. Fuel Processing Technology, 131(2): 203–212.

Dutt, K., and Soni, R. K. 2013. A review on synthesis of value added products from polyethylene terephthalate (PET) waste. Polymer Science - Series B, 55(8): 430–452.

Evode, N., Qamar, S. A., Bilal, M., Barceló, D., and Iqbal, H. M. 2021. Plastic waste and its management strategies for environmental sustainability. Case Studies in Chemical and Environmental Engineering, 4(1): 100-112.

Farzi, A., Dehnad, A., and Fotouhi, A. F. 2019. Biodegradation of polyethylene terephthalate waste using Streptomyces species and kinetic modeling of the process. Biocatalysis and Agricultural Biotechnology, 17(5): 25–31.

George, N., and Kurian, T. 2014. Recent developments in the chemical recycling of postconsumer poly(ethylene terephthalate) Waste. Industrial and Engineering Chemistry Research, 53(37): 14185–14198.

Geyer, B., Lorenz, G., and Kandelbauer, A. 2016. Recycling of poly(ethylene terephthalate) – A review focusing on chemical methods. Express Polymer Letters, 10(7): 559–586.

Geyer, R. 2020. Production, use, and fate of synthetic polymers. In Plastic Waste and Recycling, pp. 13–32, Elsevier.

Ghasemi, M. H., Neekzad, N., Ajdari, F. B., Kowsari, E., and Ramakrishna, S. 2021. Mechanistic aspects of poly(ethylene terephthalate) recycling–toward enabling high quality sustainability decisions in waste management. Environmental Science and Pollution Research, 28(32): 43074–43101.

Heidenreich, S., and Foscolo, P. U. 2015. New concepts in biomass gasification. Progress in Energy and Combustion Science, 46(5): 72–95.

Henson, R. N. 2015. Analysis of variance (ANOVA). Brain Mapping: an encyclopedic reference. Elsevier,22(3): 477-481.

Imran, M., Kim, B. K., Han, M., Cho, B. G., and Kim, D. H. 2010. Sub-and supercritical glycolysis of polyethylene terephthalate (PET) into the monomer

bis(2-hydroxyethyl) terephthalate (BHET). Polymer Degradation and Stability, 95(9): 1686–1693.

Information, N. C. for B. 2021. PubChem compound summary. National Center for Biotechnology Information Bethesda, pp.23-33, MD, USA.

Islam, M. S., Islam, Z., Hasan, R., and Islam Molla Jamal, A. H. M. S. 2023. Acidic hydrolysis of recycled polyethylene terephthalate plastic for the production of its monomer terephthalic acid. Progress in Rubber, Plastics and Recycling Technology, 39(1): 12–25.

Kandasamy, S., Subramaniyan, A., Ramasamy, G., Ahamed, A. R., Manickam, N., and Dhandapani, B. 2020. Study of alkaline hydrolysis of post consumed polyethylene terephthalate waste. AIP Conference Proceedings,8(3): 22-40.

Kanhar, A. H., Chen, S., and Wang, F. 2020. Incineration fly ash and its treatment to possible utilization: A review. Energies, 13(24):98-90.

Kazemi, M., Faisal Kabir, S., and Fini, E. H. 2021. State of the art in recycling waste thermoplastics and thermosets and their applications in construction. Resources, Conservation and Recycling, 174(4): 105-111.

Khalaf, H. I., and Hasan, O. A. 2012. Effect of quaternary ammonium salt as a phase transfer catalyst for the microwave depolymerization of polyethylene terephthalate waste bottles. Chemical Engineering Journal, 192(8): 45–48.

Kim, B. K., Kim, D., Cho, Y., and Han, M. 2008. Chemical recycling of poly(ethylene terephthalate) using a new hybrid process. Journal of Chemical Engineering of Japan, 41(9): 923–928.

Kim, H., and Lee, J. Y. (2020). Emerging concerns about microplastic pollution on groundwater in South Korea. Sustainability (Switzerland), 12(13):67-80.

Kosmidis, V. A., Achilias, D. S., and Karayannidis, G. P. 2001. Poly(ethylene terephthalate) recycling and recovery of pure terephthalic acid. Kinetics of a phase transfer catalyzed alkaline hydrolysis. Macromolecular Materials and Engineering, 286(10): 640–647.

Lear, G., Kingsbury, J. M., Franchini, S., Gambarini, V., Maday, S. D. M., Wallbank, J. A., Weaver, L., and Pantos, O. 2021. Plastics and the microbiome: impacts and solutions. Environmental Microbiomes, 16(1): 1–19.

Li, W. C., Tse, H. F., and Fok, L. 2016. Plastic waste in the marine environment: A review of sources, occurrence and effects. Science of the Total Environment, 566–567(3): 333–349.

Liu, N., Ma, Y. S., Shu, K. W., Wu, B., and Zhang, D. 2014. Catalysis investigation of pet depolymerization with brønsted acidic ionic liquid under microwave irradiation. Advanced Materials Research, 893(5): 23–26.

Lorenzetti, C., Manaresi, P., Berti, C., and Barbiroli, G. 2006. Chemical recovery of useful chemicals from polyester (PET) waste for resource conservation: A survey of state of the art. Journal of Polymers and the Environment, 14(1): 89–101.

Makarichi, L., Jutidamrongphan, W., and Techato, K. anan. 2018. The evolution of waste-to-energy incineration: A review. Renewable and Sustainable Energy Reviews, 91(7): 812–821.

Mandal, S., and Dey, A. 2019. PET Chemistry. In Recycling of Polyethylene Terephthalate Bottles, pp. 1–22, William Andrew Publishing.

Mohsin, M. A., Alnaqbi, M. A., Busheer, R. M., and Haik, Y. 2018. Sodium Methoxide Catalyzed Depolymerization of Waste Polyethylene Terephthalate Under Microwave Irradiation. Catalysis in Industry, 10(1): 41–48.

Mukrimaa, S. S., Nurdyansyah, Fahyuni, E. F., YULIA CITRA, A., Schulz, N. D.,., Taniredja, T., Faridli, E. M., and Harmianto, S. 2016. Jurnal Penelitian Pendidikan Guru Sekolah Dasar, 6(6): 128.

Mulvaney, D., Richards, R. M., Bazilian, M. D., Hensley, E., Clough, G., and Sridhar, S. 2021. Progress towards a circular economy in materials to decarbonize electricity and mobility. Renewable and Sustainable Energy Reviews, 137(1): 110-114.

Myren, T. H., Stinson, T. A., Mast, Z. J., Huntzinger, C. G., and Luca, O. R. 2020. Chemical and electrochemical recycling of end-use poly (ethylene terephthalate)(PET) plastics in batch, microwave and electrochemical reactors. Molecules, 25(12): 27-42.

Nanda, S., and Berruti, F. 2021. Thermochemical conversion of plastic waste to fuels: a review. Environmental Chemistry Letters, 19(1): 123–148.

Okan, M., Aydin, H. M., and Barsbay, M. 2019. Current approaches to waste polymer utilization and minimization: a review. Journal of Chemical Technology and Biotechnology, 94(1): 8–21.

Padhan, R. K., Gupta, A. A., Badoni, R. P., and Bhatnagar, A. K. 2013. Poly(ethylene terephthalate) waste derived chemicals as an antistripping additive for bitumen - An environment friendly approach for disposal of environmentally hazardous material. Polymer Degradation and Stability, 98(12): 2592–2601.

Park, R., Sridhar, V., and Park, H. 2020. Taguchi method for optimization of reaction conditions in microwave glycolysis of waste PET. Journal of Material Cycles and Waste Management, 22(3): 664–672.

Paszkiewicz, S., Szymczyk, A., ŠpitalskýZ., Soccio, M., Mosnáček, J., Ezquerra, T. A., and Rosłaniec, Z. 2012. Electrical conductivity of poly(ethylene terephthalate)/expanded graphite nanocomposites prepared by in situ polymerization. Journal of Polymer Science, Part B: Polymer Physics, 50(23): 1645–1652.

Pham, D. D., and Cho, J. 2021. Low-energy catalytic methanolysis of poly(ethyleneterephthalate). Green Chemistry, 23(1): 511–525.

Pingale, N. D., and Shukla, S. R. 2008. Microwave assisted ecofriendly recycling of poly (ethylene terephthalate) bottle waste. European Polymer Journal, 44(12): 4151–4156.

Pinter, E., Welle, F., Mayrhofer, E., Pechhacker, A., Motloch, L., Lahme, V., ... and Tacker, M. 2021. Circularity study on PET bottle-to-bottle recycling. Sustainability, 13(13): 73-79.

Porta, R. 2019. The plastics sunset and the bio-plastics sunrise. Coatings, 9(8): 90-99.

Pudack, C., Stepanski, M., and Fässler, P. 2020. PET Recycling – Contributions of Crystallization to Sustainability. Chemie-Ingenieur-Technik, 92(4): 452–458.

Ragaert, K., Delva, L., and Van Geem, K. 2017. Mechanical and chemical recycling of solid plastic waste. Waste Management, 69(2): 24–58.

Raheem, A. B., Noor, Z. Z., Hassan, A., Abd Hamid, M. K., Samsudin, S. A., and Sabeen, A. H. 2019a. Current developments in chemical recycling of post-consumer polyethylene terephthalate wastes for new materials production: A review. Journal of Cleaner Production, 225(7): 1052–1064.

Raheem, A. B., Noor, Z. Z., Hassan, A., Abd Hamid, M. K., Samsudin, S. A., and Sabeen, A. H. 2019b. Current developments in chemical recycling of post-consumer polyethylene terephthalate wastes for new materials production: A review. Journal of Cleaner Production, 225(3): 1052–1064.

Rajmohan, K. V. S., Ramya, C., Raja Viswanathan, M., and Varjani, S. 2019. Plastic pollutants: effective waste management for pollution control and abatement. Current Opinion in Environmental Science and Health, 12(4): 72–84.

Rodrigues, M. O., Gonçalves, A. M. M., Gonçalves, F. J. M., Nogueira, H., Marques, J. C., and Abrantes, N. 2018. Effectiveness of a methodology of microplastics isolation for environmental monitoring in freshwater systems. Ecological Indicators, 89(1): 488–495.

Rosenboom, J. G., Langer, R., and Traverso, G. 2022. Bioplastics for a circular economy. Nature Reviews Materials, 7(2): 117–137.

Rubio Arias, J. J., Barnard, E., and Thielemans, W. 2022. Ultrafast Simultaneous and Selective Depolymerization of Heterogeneous Streams of Polyethylene Terephthalate and Polycarbonate: Towards Industrially Feasible Chemical Recycling. ChemSusChem, 15(15):1–18.

Saifuddin Syed Salahuddin, S., and Suganchand Zambani, S. 2020. Utilisation of Waste Hdpe Plastic in Manufacturing Plastic Sand Bricks. International Research Journal of Engineering and Technology, 4(4): 3938–3942.

Salaudeen, S. A., Arku, P., and Dutta, A. 2019. Gasification of plastic solid waste and competitive technologies. In Plastics to Energy, pp. 269-293. William Andrew Publishing.

Salazar-Beltrán, D., Hinojosa-Reyes, L., Palomino-Cabello, C., Turnes-Palomino, G., Hernández-Ramírez, A., and Guzmán-Mar, J. L. 2018. Determination of phthalate acid esters plasticizers in polyethylene terephthalate bottles and its correlation with some physicochemical properties. Polymer Testing, 68(6): 87–94.

Salminen, P. 2013. Using recycled polyethylene terephthalate (PET) in the production of bottle trays. PhD thesis, Arcada. 97.

Santos, S. M., Nobre, C., Brito, P., and Gonçalves, M. 2023. Brief Overview of Refuse-Derived Fuel Production and Energetic Valorization: Applied Technology and Main Challenges. Sustainability, 15(13): 10342.

Sherwood, J. 2019. Closed-Loop Recycling of Polymers Using Solvents : Remaking plastics for a circular economy. Johnson Matthey Technology Review, 64(1): 4–15.

Shojaei, B., Abtahi, M., and Najafi, M. 2020. Chemical recycling of PET: A stepping-stone toward sustainability. Polymers for Advanced Technologies, 31(12): 2912–2938.

Shukla, S. R., and Harad, A. M. 2006. Aminolysis of polyethylene terephthalate waste. Polymer Degradation and Stability, 91(8): 1850–1854.

Siddiqui, M. N., Achilias, D. S., Redhwi, H. H., Bikiaris, D. N., Katsogiannis, K. A. G., and Karayannidis, G. P. 2010. Hydrolytic depolymerization of PET in a microwave reactor. Macromolecular Materials and Engineering, 295(6): 575–584.

Siddiqui, M. N., Redhwi, H. H., Al-Arfaj, A. A., and Achilias, D. S. 2021. Chemical recycling of pet in the presence of the bio-based polymers, pla, phb and pef: A review. Sustainability (Switzerland), 13(19):76-87.

Sinha, V., Patel, M. R., and Patel, J. V. 2010. Pet waste management by chemical recycling: A review. Journal of Polymers and the Environment, 18(1): 8–25.

Sobkowicz-Kline, M., Budhlall, B. M., and Mead, J. L. 2017. Synthetic resins and plastics. Handbook of industrial chemistry and biotechnology,7(7): 1397-1462.

Stanica-Ezeanu, D., and Matei, D. 2021. Natural depolymerization of waste poly(ethylene terephthalate) by neutral hydrolysis in marine water. Scientific Reports, 11(1): 1–7.

Thiounn, T., and Smith, R. C. 2020. Advances and approaches for chemical recycling of plastic waste. Journal of Polymer Science, 58(10): 1347–1364.

Thompson, R. C., Moore, C. J., Saal, F. S. V., and Swan, S. H. 2009. Plastics, the environment and human health: Current consensus and future trends. Philosophical Transactions of the Royal Society B: Biological Sciences, 364(1): 2153–2166.

Tierney, J. P., and Lidström, P. 2009. Microwave Assisted Organic Synthesis. Microwave Assisted Organic Synthesis, 57(589): 1–28.

Trippe, F., Fröhling, M., Schultmann, F., Stahl, R., and Henrich, E. 2011. Techno-economic assessment of gasification as a process step within biomass-to-liquid

(BtL) fuel and chemicals production. Fuel Processing Technology, 92(11): 2169–2184.

Tsui, T. H., and Wong, J. W. C. 2019. A critical review: emerging bioeconomy and waste-to-energy technologies for sustainable municipal solid waste management. Waste Disposal and Sustainable Energy, 1(3): 151–167.

Ügdüler, S., Van Geem, K. M., Denolf, R., Roosen, M., Mys, N., Ragaert, K., and De Meester, S. 2020. Towards closed-loop recycling of multilayer and coloured PET plastic waste by alkaline hydrolysis. Green Chemistry, 22(16): 5376–5394.

Vendan, S. A., Natesh, M., Garg, A., and Gao, L. 2018. Confluence of Multidisciplinary Sciences for Polymer Joining. Confluence of Multidisciplinary Sciences for Polymer Joining,7: 1–147.

Vermeulen, I., Van Caneghem, J., Block, C., Baeyens, J., and Vandecasteele, C. 2011. Automotive shredder residue (ASR): Reviewing its production from end-of-life vehicles (ELVs) and its recycling, energy or chemicals' valorisation. Journal of Hazardous Materials, 190(3): 8–27.

Wakabayashi, N., Kojima, T., and Funazukuri, T. 2012. Recovery of terephthalic acid and ethylene glycol from poly(ethylene terephthalate) under hydrothermal conditions of aqueous trimethylamine solution. Industrial and Engineering Chemistry Research, 51(16): 5699–5704.

Wan, B. Z., Kao, C. Y., and Cheng, W. H. 2001. Kinetics of depolymerization of poly(ethylene terephthalate) in a potassium hydroxide solution. Industrial and Engineering Chemistry Research, 40(2): 509–514.

Wang, J., and Mao, Q. 2012. Methodology Based on the PVT Behavior of Polymer for Injection Molding. Advances in Polymer Technology, 32(4): 474–485.

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.

Young, R. J., and Lovell, P. A. 2011. Introduction to polymers. pp.89-110. CRC press.

Zhang, S., Xu, W., Du, R., Zhou, X., Liu, X., Xu, S., and Wang, Y.-Z. 2022. Cosolvent-promoted selective non-aqueous hydrolysis of PET wastes and facile product separation. Green Chemistry, 24(8): 3284–3292.

APPENDICES

APPENDIX 1. FTIR chart for all experimants

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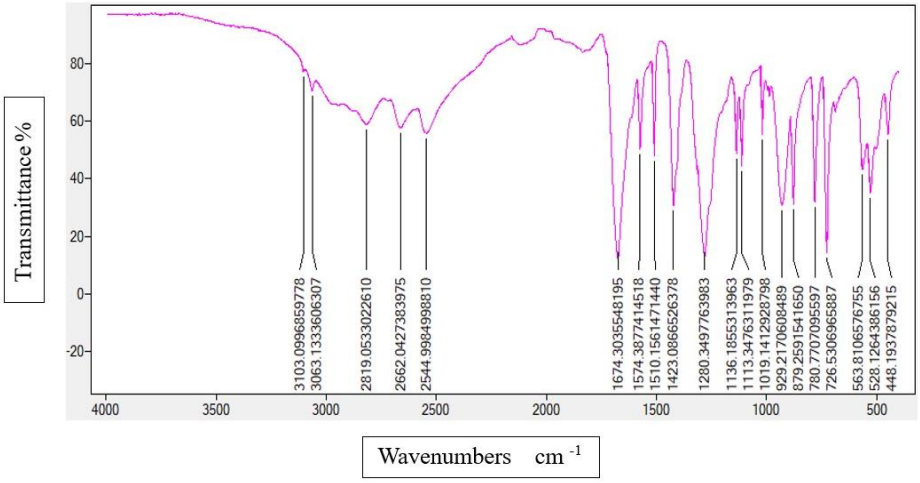

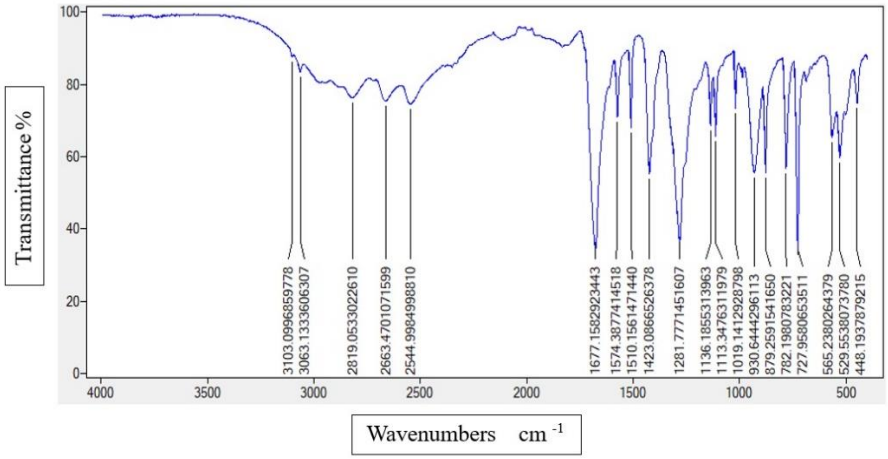

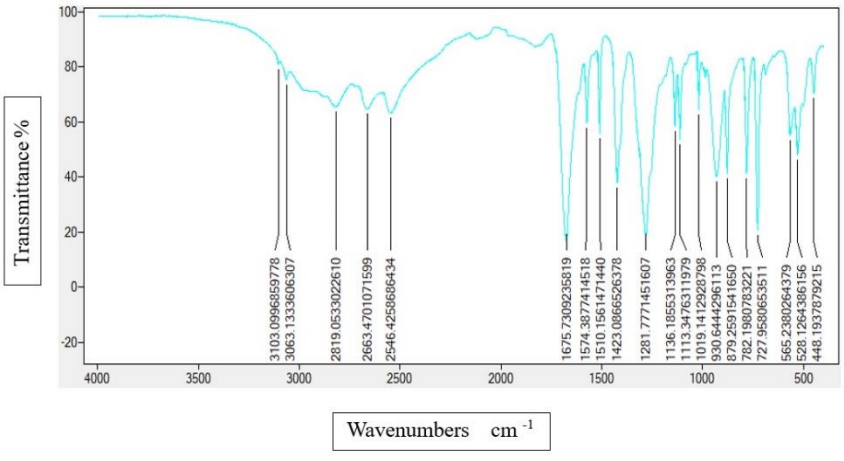

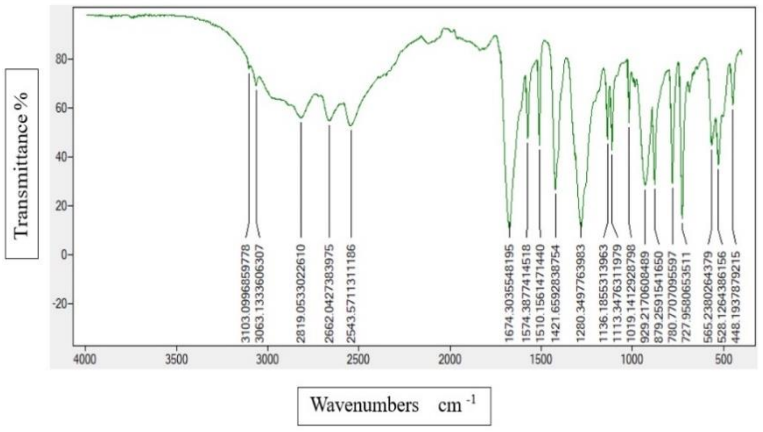
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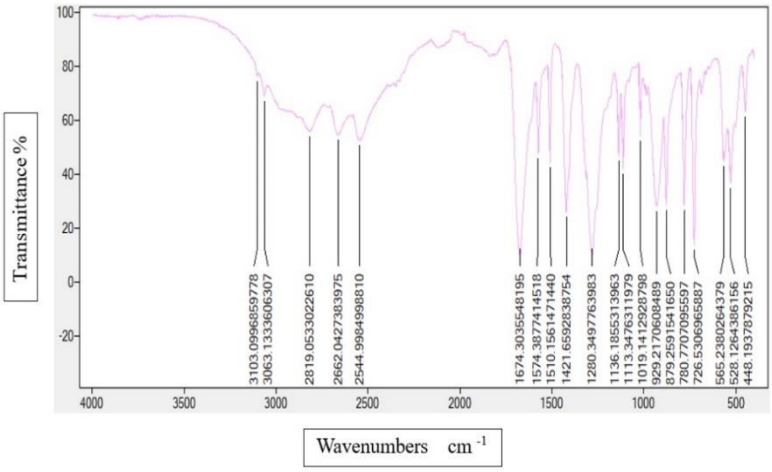
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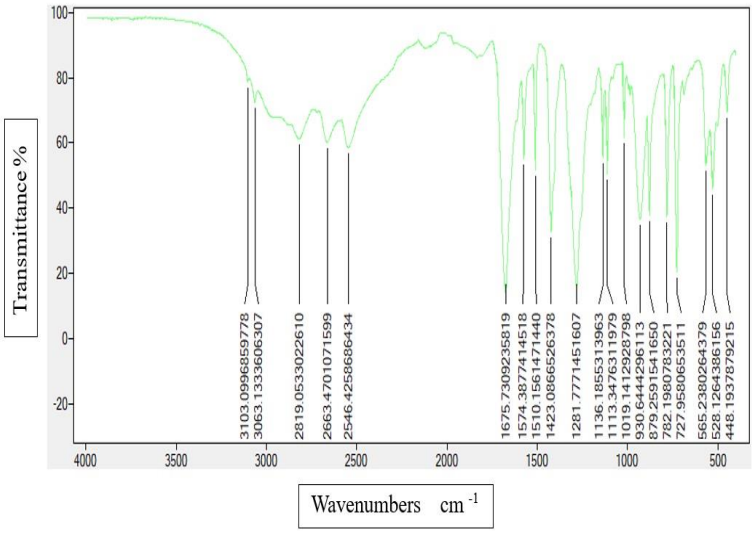
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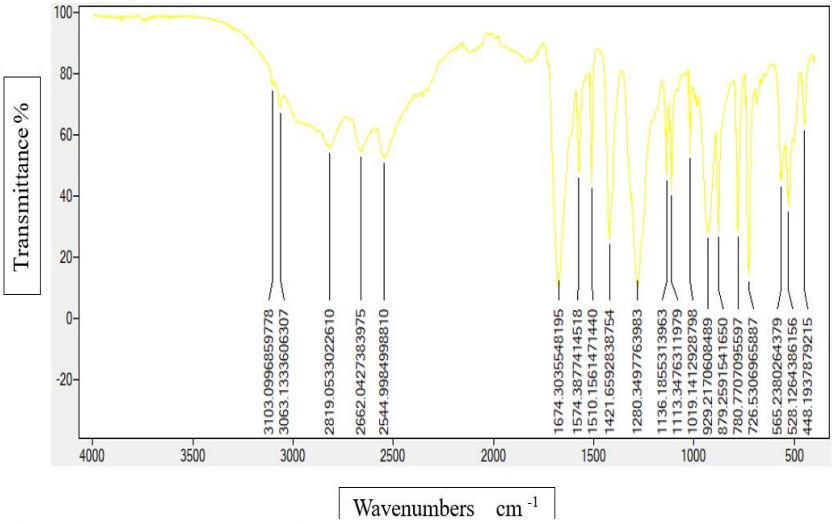
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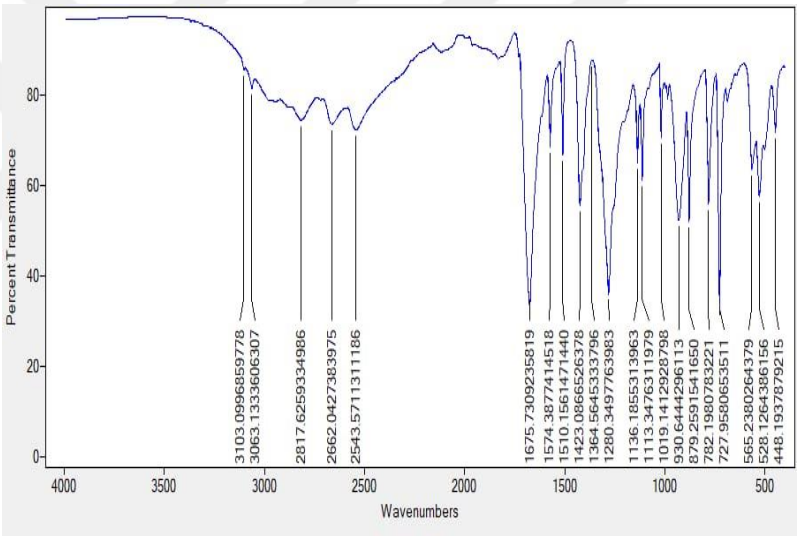
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