LITERATURE SURVEY
2.1 Chemical Recycling (Tertiary Recycling)

Great attention is paid to chemical recycling, which basically means the recovery of monomers or partial depolymerization to oligomers and other chemical substances which produce useful chemicals from PET waste. Poly (ethylene terephthalate) is very vulnerable to chemical degradation. PET is polyester with functional ester groups that can be cleaved by some reagents, such as water (hydrolysis), alcohols (alcoholysis), glycols (glycolysis), and amines (aminolysis).

The solvolytic chemical recycling of PET waste is schematically represented below in Fig. 2.1.

Fig. 2.1: The chemical recycling of PET waste by solvolysis
2.1.1. Hydrolysis

Hydrolysis is a method of PET waste recycling in which PET is reacted with water in acidic, basic or neutral condition, leading to complete depolymerization to obtain its monomers, terephthalic acid (TPA) and ethylene glycol (EG). The main disadvantage of this method is the use of high temperature (200–250 °C) and pressure (1.4–2.0 MPa) as well as the long time needed for complete depolymerization. Commercially, hydrolysis is not widely used, because of the cost associated with purification of the recycled TPA. If some of the limitations of hydrolysis can be addressed, then it may provide economically feasible route.

Hydrolysis of PET waste can be carried out as a) Alkaline hydrolysis, b) Acid hydrolysis and c) Neutral hydrolysis.

2.1.1. a. Alkaline hydrolysis

Alkaline hydrolysis of PET waste is usually carried out using NaOH or KOH to get the corresponding terephthalate salt, which on acidification gives monomer TPA (Fig.2.2). The process generally runs for 3-5 h at temperature of 210-250 °C, under pressure of 1.4-2 MPa (Alter, 1986).

Kao et al. investigated the alkaline hydrolysis of PET waste by using DSC and TGA to obtain TPA (Kao et al., 1998). Furthermore, detailed reaction kinetics of PET depolymerization in a KOH solution was investigated using a pressurized autoclave [Wan B-Z, et al., 2001].

Chemical recycling of PET flakes to TPA and oxalic acid was investigated by simultaneous hydrolysis and oxygen oxidation in concentrated NaOH. PET flakes were hydrolyzed to sodium terephthalate and ethylene glycol (EG) in NaOH solutions before oxygen introduction. Because sparingly soluble sodium terephthalate in concentrated NaOH solutions was stable to oxidation, the TPA yield was approximately 100 mol % under all conditions. Thus, apart from monomer TPA a valuable byproduct (oxalic acid) was obtained (Yoshioka et al. 2003).
Ramsden and Phillips investigated the factors such as temperature, time and alkali concentration influencing the kinetics of the alkaline depolymerization of PET in NaOH solution. They also reported that the choice of solvent plays an important role in the alkaline depolymerization of PET. Strong solvent-polymer interactions can facilitate the depolymerization by causing swelling to mitigate diffusion effects, and strong solvent-solvent interaction can enhance the nucleophilicity of the hydroxide ion (Ramsden and Phillips, 1996).

![Diagram of PET depolymerization](image_url)

**Fig. 2.2:** Alkaline hydrolysis of PET waste

The recovery of TPA and other monomeric components from PET/polyamide 6 polymeric mixtures has been reported. In the first stage, the mixture is heated in an aqueous solution of sodium or potassium hydroxide; most favourable results are achieved
at temperatures of 210-250 °C under autogenic pressure. If hydroxide solutions of a concentration of 3-10 wt % are used, then the reaction time amounts to 3-5 h. The quantity of alkali used is dependent on the polyester content of the polymer mixture. After the termination of the reaction, the mixture is filtered in order to remove the insoluble residue, and then a strong mineral acid is added so that the dicarboxylic acid being formed is released. The generated caprolactam and EG are separated by distillation or are salted out using NaCl (Lazarus et al. 1967).

PET hydrolysis in aqueous alkaline solution was investigated by Karayannidis et al. Thereaction took place with a constant NaOH concentration and different reaction-time intervals and temperatures. A great increase in the TPA yield on increasing the reaction temperature was observed. At the highest-studied temperature of 200 °C a TPA yield of 98% was obtained in only 1 h (Karayannidis et al. 2002).

Namboori and Haith carried out comparative study of the reactivity of hydroxide and various alkoxide anions by determining percentage weight loss of PET fiber. Regardless of the basicity of the anions, the order of reactivity was found to be hydroxide < tertbutoxide < sec-propoxide < methoxide < ethoxide. This observed order follows the nucleophilicity of the bases, and the relatively lower reactivity of sec-propoxide and tertbutoxide is assumed to be due to steric retardation during the equilibrium reactions (Namboori and Haith, 1968).

**PET alkaline hydrolysis in non aqueous alkaline solutions**

Oku and Yamada carried out alkali decomposition of PET waste with sodium hydroxide in non aqueous ethylene glycol at 150 °C for 80 min or 180 °C for 15 min to convert it quantitatively to disodium terephthalate (Na₂-TPA) and EG. The disodium salt was precipitated quantitatively in pure state from the EG solution and separated readily. The other product EG, being the same component to the solvent, remains in the solution and can be obtained after distillation. The rate of decomposition was significantly accelerated by the addition of ethereal solvents to EG, such as dioxane, tetrahydrofuran, and dimethoxyethane. (Oku and Yamada, 1997). One possible explanation is that ethers accelerate the percolation of hydroxide ions and increase their ionic strength and, therefore, the decomposition of PET was increased.
PET hydrolysis in non aqueous alkaline solution was investigated by Karayannidis et al. The reaction took place in an autoclave with a nonaqueous solution of KOH in methyl Cellosolve. Methyl Cellosolve (CH$_3$-O-CH$_2$-CH$_2$-OH) is a chemical compound combining the properties of ether together with those of an alcohol. The ether part led to swelling of the PET solid and the alcoholic part supported the action of OH$^-$ in destroying the chemical structure of PET during depolymerization (PET surface was easily attacked by alcohols) (Karayannidis et al., 2002). The reaction temperature was 120 °C and the reaction time was 2.5 h. A sharp increase in the TPA yield and the rate of hydrolysis was observed, as the concentration increased, which tended to be smoother with KOH concentrations higher than 4 M. The increase in the solution viscosity inhibits the removal of TPA-K$_2$ from the PET surface (TPA-K$_2$ is insoluble in methyl cellosolve).

Microwave-assisted hydroglycolysis of poly(ethylene terephthalate) using an excess of methanol, ethanol, 1-butanol, 1-pentanol, and 1-hexanol in the presence of different simple basic catalysts, namely, potassium hydroxide, sodium hydroxide, sodium acetate, and zinc acetate, is reported (Nikje and Nazari, 2006). Reactions were performed at short times without any side reactions, namely, oxidation of ethylene glycol. The products, terephthalic acid and ethylene glycol, were obtained in their pure form with sufficiently high yields with potassium hydroxide.

Broccatelli carried out recycling of PET bottle waste by reacting it with reagent consisting of one or more metal salts of weaker acid than TPA and of EG until a water soluble intermediate is obtained. (Broccatelli, 2004)

**PET alkaline hydrolysis using phase transfer catalyst**

Phase transfer catalyst (PTC) is a catalyst that facilitates the migration of a reactant from one phase into another phase where reaction occurs. Ionic reactants are often soluble in an aqueous phase but insoluble in an organic phase in the absence of the phase transfer catalyst. The catalyst functions like a detergent for solubilizing the salts into the organic phase.

By using a PTC process, one can achieve faster reactions, obtain higher conversions or yields, make fewer byproducts, eliminate the need for expensive or
dangerous solvents that will dissolve all the reactants in one phase, eliminate the need for expensive raw materials and/or minimize the waste problems.

Polk et al. carried out depolymerization of PET, Nylon 66 and Nylon 46 in alkaline solutions at low temperatures and atmospheric pressure. A method was developed for the depolymerization of PET fibre, which involved the use of quarternary ammonium salt as phase-transfer catalyst in saponification processes at atmospheric pressure. Phenyltrimethylammonium chloride, hexadecyltrimethylammonium bromide, trioctylmethylammonium chloride and trioctylmethylammonium bromide were found to be effective catalysts for the depolymerization of PET in 5% aqueous sodium hydroxide solution at temperature as high as 80°C and atmospheric pressure to form TPA in yields as high as 93% (Polk et al., 1999).

Karayannidis et al. studied the kinetics of phase transfer catalyzed depolymerization reaction of PET taken from post consumer soft drink bottles (Karayannidis et al., 2001). The effect of temperature, alkali concentration, PET particle size, PET concentration and catalyst to PET ratio on the TPA yield were investigated. The rate of hydrolysis was increased with the increase in NaOH concentration. They also observed that PET degradation was increased by decreasing the particle size. Flakes with decreased particle size have increased surface area available for the reaction. Thus, the reaction rate is increased and greater conversions can be obtained.

Lopez-fonseca et al. examined various quarternary ammonium/phosphonium salts for alkaline hydrolysis of PET waste (Lopez-fonseca et al., 2008). Tributylhexadecylphosphonium bromide (3Bu4DPB) was discovered to be an active phase transfer catalyst for PET depolymerization or chemical recovery of the monomers by alkaline hydrolysis since it accelerated the reaction rate considerably. It is thought that this quarternary phosphonium salt acts as a shuttling agent by extracting the OH− anion from the aqueous phase into the organic interfacial region (the surface of solid PET flakes) where the anion can freely react with the organic reactant. Thus, noticeable conversion of PET with low catalyst concentration and energy at relatively low temperature ranging between 70 and 80 °C was attained. A kinetic model considering the reaction rate to be first order with respect to PET, NaOH, and PTC concentration satisfactorily described the kinetics of the alkaline hydrolysis. Both non-catalysed and
phase transfer catalysed processes presented roughly the same activation energy. The increase in reaction rate in the presence of quaternary phosphonium salt (about 130–190 times greater) was attributed to the much higher value for the pre-exponential factor.

PET was hydrolyzed using alkaline solution under atmospheric pressure using PTC (Parikh et al., 2007). Among the catalyst tested, benzalkonium chloride (BKC) was found to be the most effective. Complete conversion of PET with low catalyst concentration, alkali concentration and temperature was achieved.

2.1.1. b. Neutral hydrolysis

Neutral Hydrolysis is carried out with the use of hot water or steam. The process usually runs in high-pressure autoclaves at temperatures of 200–300 °C and pressures of 1–4 MPa and in excesswater. It has been confirmed that PET hydrolysis proceeds significantly faster in the molten state than in the solid one; therefore, it is advantageous to carry out recycling using this method at temperatures higher than 245 °C (Paszhun and spychaj, 1997). The ratio by weight of PET to water is from 1:2 to 1:12. The main products formed are EG and TPA. TPA is separated from the post reaction mixture by filtration, while a substantial volume of diluted EG is recovered through extraction or by distillation.

A systematic study of the hydrolytic degradation of PET by Ravens et al. in the early 60s revealed that the hydrolytic scission of polyester chains above their glass transition temperature was an autocatalytic reaction and the process was a rate-controlled chemical reaction (Ravens et al., 1961). Each chain scission uses one water molecule and creates one carboxylic end group. Hence, the extent of reaction can be followed by measuring the number of carboxyl ends present when varying the hydrolytic degradation time. The built-up of terminal acid groups is responsible of autocatalytic phenomena that can explain the autoaccelerating character of the reaction. According to this interpretation, the reaction is catalyzed by hydrogen ions produced by the carboxyl end groups.

PET is a semicrystalline thermoplastic polyester, thus built of amorphous and crystalline regions. Water absorption and thus chain scission are only possible in the amorphous phase, owing to the impermeability of crystals. The chain segments
previously entrapped in the amorphous phase are then liberated and become sufficiently mobile to enter into the crystalline phase. The drastic increase in the crystallinity cannot be ignored in a kinetic study of hydrolysis. Allene et al. observed a difference in the degradation rates associated with differences in the initial crystallinity of the materials (Allene et al., 1991). The strong influence of crystallinity on the rate of hydrolytic degradation of PET is believed to be due to the fact that crystallites act as barriers to moisture and oxygen diffusion. The initial crystallinities of PET determine the degradation rates as well as the nature of the degradation conditions.

An effective five-stage process of neutral hydrolysis of PET to EG and TPA of a purity required for the synthesis of the new polymer has been patented (Tustin et al., 1995). PET is hydrolyzed at temperatures of 200-280 °C. After cooling the postreaction mixture to 70-100 °C, the solid product of the process is filtered and dried at temperatures of 25-199 °C. EG is recovered from the filtrate as a result of two-stage distillation. The solid product of hydrolysis is heated with water at temperatures of 310-370 °C and after cooling TPA is obtained. The purity of the recovered TPA and EG allows their application in the production of high-quality homo- and copolymers and does not exclude their use in the manufacture of bottles and fibres.

Neutral hydrolysis of waste PET in the presence of xylene was investigated by Guclu et al. The organic solvent made it possible to employ very low amounts of water, lower temperatures and pressures and provided concentrated EG solutions yielding intermediates suitable for PET preparation (Guclu et al., 2003).

In comparison to acid and alkaline hydrolysis, neutral hydrolysis has the main advantage that formation of substantial amounts of inorganic salts, which are difficult to dispose of, is avoided. Therefore, it can be considered as more environmentally friendly and a growing interest in this technology is expected. Its main drawback is that all mechanical impurities present in PET are left in the TPA, thus the product can be considered of lower purity than the product of acid or alkaline hydrolysis.

2.1.1. c. Acid hydrolysis

Although the application of other concentrated mineral acids (e.g., phosphoric or nitric acid) is permissible, acid hydrolysis is performed most frequently using
concentrated sulphuric acid (minimum 87% by weight) (Fig.2.3). These acid levels allow the process to take place in a pressure-less apparatus, typically without requiring external energy supply (Brown and O’Brien, 1976; Pusztaszeri, 1982; Sharma et al., 1985).

Mehrabzadeh et al. reported acidic hydrolysis of PET using sulphuric acid. The effect of different parameters, such as acid concentration, time, temperature and PET particle size on the decomposition and reaction yield was investigated (Mehrabzadeh et al., 2000). They showed that at temperature range between 130-170 °C the rate of degradation of PET increases. 

![PET Waste](image)

**Fig.2.3.** Acid hydrolysis of PET waste

Kinetics of hydrolysis of PET powder in sulphuric acid by core shrinking model was investigated (Yoshioka et al., 2001). PET powder from waste bottles was degraded at atmospheric pressure in 3-9 M sulphuric acid below 150-190 °C for 12 h to clarify the mechanism for a feedstock recycle process. TPA and EG were produced by the acid-catalyzed hydrolysis of PET in sulphuric acid. The TPA yield agreed with the degree of
hydrolysis of PET, but the EG yield decreased with increasing sulphuric acid concentration because of carbonization of EG. The kinetics of hydrolysis of PET in sulphuric acid was explained by a modified shrinking-core model for the chemical reaction control, in which the effective surface area is proportional to the degree of hydrolyzed PET.

Post-consume PET was hydrolyzed with commercial sulphuric acid (96%) with varying reaction times (5-120 min) (Rubira et al., 2006). The structure of the material obtained was analyzed by \(^{13}\)C NMR, DSC, and WAXD and the results were correlated with reaction time. \(^{13}\)C NMR shows a decrease in chain size with reaction time and an increase in the number of carboxyl groups at the end of the chains. The correlation of DSC and WAXD data indicates the presence of structures of different sizes and an increase in crystallinity with reaction time.

EG was recovered from the remaining filtrate through extraction with organic solvents, e.g., trichloroethylene (Brown and O’Brien, 1976). Another method for EG recovery is based on the introduction into the filtrate of sodium sulphate so as to obtain a saturated solution. EG salting out takes place, forming a separate organic layer.

A substantial drawback of PET hydrolysis by concentrated sulphuric acid is the high corrosivity of the reaction system and the generation of large quantities of waste inorganic salts and aqueous wastes. Yoshioka et al. conducted a minimization trial of the last two inconveniences (Yoshioka et al. 1994). Diluted solutions of H\(_2\)SO\(_4\) (<67.7 wt %) were used for this purpose; the sulphuric acid can be recovered and reused in the process. However, this requires the prolongation of reaction time to 1-6 h, and the process runs at much higher temperatures ~150°C; also the high pressure apparatus used should have a large volume due to the necessity to use an excess of diluted acid.

**PET hydrolysis using ionic liquid**

The hydrolysis of PET was studied (Fig.2.4) using ionic liquid 1-n-butyl-3-methylimidazolium chloride ([Bmim][Cl]) as solvent and acid-functionalized ionic liquid 1-methyl-3-(3-sulphopropyl)-imidazolium hydrogen sulphate ([HSO\(_3\)-pmim][HSO\(_4\)]) as catalyst (Liu et al., 2009). The effects of temperature, time, and dosages of solvent and catalyst on hydrolysis results were examined. Under the optimum conditions of reaction
temperature 170 °C and time 4.5 h, the conversion of PET and the yield of TPA were almost 100% and 88%, respectively.

![Ionic liquids](image)

**Fig.2.4.** Hydrolysis of PET waste using ionic liquids

### 2.1.2. Methanolysis

The process consists of the degradation of PET by methanol at high temperature and pressure conditions (Fig.2.5). The main products being dimethyl terephthalate (DMT) and ethylene glycol (EG), which are raw materials necessary for the production of this polymer.

The depolymerization rate is a function of temperature and of transesterification catalyst concentration when used; solubility of PET and its oligomer in reaction medium is another important factor affecting the kinetics of this process.

Methods for the conduction of methanolysis have similar basic parameters, e.g., pressures of 2-4 MPa and temperatures of 180-280 °C (Lotz et al., 1967; Marathe et al.,...
The reaction is catalysed by different transesterification catalysts like zinc acetate, magnesium acetate, cobalt acetate, and lead oxide; however, zinc acetate is the most commonly used catalyst. The depolymerisation process takes place via release of EG. Post reaction mixture DMT was precipitated out, centrifuged and then crystallized.

![PET Waste](image)

**Fig.2.5.** Methanolysis of PET waste

The degradation of PET in supercritical methanol was investigated with the aim of developing a process for chemical recycling of waste plastics (Goto et al., 2002). A batch reactor was used at temperatures of 300-350 °C under an estimated pressure of 20 MPa for a reaction time of 2–120 min. The reaction products were analyzed using size-exclusion chromatography, gas chromatography–mass spectrometry, and reversed-phase liquid chromatography. The molecular weight distribution of the products was obtained as a function of reaction time. The yield of DMT and EG at 330 °C became lower than those at 300 °C at a later time because of secondary reactions. 2-methoxy ethanol and diethylene glycol, which are the secondary products from EG, increased with reaction time.
time and their yields are higher at higher temperature. These reactions produce water which works as a reactant in the production of monomethyl ester of TPA.

Methanolytic depolymerization of PET was carried out in a stainless stirred autoclave at temperatures of 250–270 °C, pressures of 8.5–14.0 MPa, and with a weight ratio of methanol to PET from 3 to 8 (Yang et al., 2002). The solid products mainly composed of DMT and small amounts of methyl-(2-hydroxyethyl) terephthalate (MHET), dimers and oligomers were analyzed by high performance liquid chromatography (HPLC) (Fig.2.6). The liquid products composed of ethylene glycol and methanol were analyzed by gas chromatography (GC). It was found that both the yield of DMT and the degree of PET depolymerization were seriously influenced by the temperature, weight ratio of methanol to PET, and reaction time, whilst the pressure has insignificant influence when it is above the critical point of methanol. The optimal depolymerization conditions are temperature of 260–270 °C, pressure of 9.0–11.0 MPa, and the weight ratio (methanol to PET) from 6 to 8.

![Chemical structures](image)

**Fig.2.6.** Oligomers obtained during methanolysis PET waste
Kim et al. proposed a new hybrid process consisting of glycolysis/methanolysis and then a vapor methanolysis process to obtain DMT and EG in the depolymerization of waste PET (Kim et al., 2008). Zinc acetate was used to catalyze the reactions. They found that the depolymerization rate increased remarkably when glycolysis and methanolysis reactions were simultaneously carried out than when the glycolysis reaction was performed alone. They also investigated the effect of major process variables such as reaction pressure, reaction temperature, reaction time, amount of EG, and methanol feed rate on process performance. They found that methanolysis has a greater role than glycolysis in the glycolysis/methanolysis step and the DMT yield has a maximum at a reaction temperature of 240 °C and EG/PET mole ratio of 0.52, and increases with reaction pressure.

Methanolic pyrolysis (methanolysis) of PET taken from waste soft-drink bottles, under microwave irradiation, was proposed as a recycling method with substantial energy saving (Siddiqui et al., 2012). The reaction was carried out with methanol with and without the use of zinc acetate as catalyst in a sealed microwave reactor in which the pressure and temperature were controlled and recorded. Experiments under constant temperature or microwave power were carried out at several time intervals. The main product DMT was analyzed and identified by FTIR and DSC measurements. It was found that PET depolymerization, was favoured by increasing temperature, time and microwave power. High degrees of depolymerization were also obtained at temperatures near 180 °C and at microwave power higher than 150 W. Most of the degradation was found to occur during the initial 5–10 min.

A common problem found in methanolysis is the separation of EG from DMT and catalyst residues while methanol is easily removed due its low boiling point. If water perturbs the process, it poisons the catalyst and forms various azeotropes. However, the main disadvantage is associated with the trend of all of the new PET production processes to use TPA instead of DMT as the raw material. The conversion of the DMT produced by hydrolysis to TPA also adds considerable cost to the methanolysis process.
**Methanolysis using ionic liquids**

The methanolysis of PET was studied using ionic liquid 1-n-butyl-3-methylimidazolium chloride [Bmim][Cl] as solvent and zinc acetate as catalyst (Liu et al., 2009). A great increase in PET conversion was observed with increasing [Bmim][Cl] concentration and reaction temperature. Under the optimum conditions of reaction temperature 160 °C, reaction time 3h, solvent:PET:: 2:1 the conversion of PET and the yield of DMT were almost 100% and ≥88% respectively. After easily separated from the product, the system of solvent and catalyst was reused 8 times without obvious decrease in the conversion of PET and yield of DMT.

2.1.3. Glycolysis

The most important method in the chemical processing of PET waste is glycolysis. This process is used widely on a commercial scale. The result of deep glycolysis by EG is primarily bis-2-(hydroxyethyl) terephthalate (BHET), which can be directly used in PET synthesis (Fig.2.7).

![Fig.2.7. Glycolysis of PET waste](image-url)
PET degradation is carried out most frequently using EG, (Fujita et al., 1985, 1986; Baliga and Wong, 1989; Vaidya and Nadkarni, 1989), diethylene glycol (DEG)(Ostrysz, 1969; Vaidya and Nadkarni, 1989; Johnson and Teeters, 1991), propylene glycol (PG)(Vaidya and Nadkarni, 1987b, 1989; Kim et al., 1995), and dipropylene glycol (Johnson and Teeters, 1991; Kim et al., 1995).

Much attention has been devoted to the glycolysis of PET by EG. The method involves the reaction of PET at temperatures in the range 180-240 °C with an excess of EG which promotes the formation of BHET. The depolymerization is carried out in the presence of a transesterification catalyst, usually zinc or lithium acetate.

PET waste was depolymerized by glycolyzing it with glycols like EG, propylene glycol (PG), and diethylene glycol (DEG) (Vaidya & Nadkarni, 1989). The extent of the glycolysis depends on the moles of the glycol present when glycolyzed on a weight basis. The extent of glycolysis was found to be the highest for EG, giving the diester, BHET. The oligomeric diols thus obtained could be polyesterified with adipic acid to get polyester polyols of different molecular weights. These polyester polyols when reacted with polymeric 4,4'-diphenyl methane diisocyanate (PMDI) gave elastomers.

PET from post-consumer soft-drink bottles was depolymerized by glycolysis in excess ethylene glycol at 190 °C in the presence of a metal acetate catalyst (Baliga and Wong, 1989). The glycolyzed products consisted mostly of the PET monomer, BHET and the dimer, and after long reaction time (up to and longer than 8 h). No other higher PET oligomers were detected in the study. After prolonged glycolysis, equilibrium was established between the monomer and the dimer and ethylene glycol, with an equilibrium constant lying between 1.13 to 1.53. Of the four metal acetates (lead, zinc, cobalt, and manganese) tested, zinc acetate was found to be the best in terms of the extent of depolymerization, that is, the relative amount of monomer formed.

PET waste was depolymerized with ethylene glycol in the presence of different catalysts, two conventional metal catalysts (zinc acetate and lead acetate) and two alkalies (sodium carbonate and sodium bicarbonate) (Shukla and Kulkarni, 2002). The results showed that the qualitative and quantitative yields of the monomer obtained with alkalies as catalysts were most comparable with the conventional heavy metal catalysts,
thus provided advantage for the recycling of polyester waste for the cause of environmental pollution abatement.

Glycolysis of polyethylene terephthalate waste fibres was carried out using excess ethylene glycol in the presence of different simple chemicals, namely, glacial acetic acid, lithium hydroxide, sodium sulphate, and potassium sulphate (Shukla and Harad, 2005). They have studied the mechanism of glycolysis of PET.

![Mechanism of glycolysis of PET waste](image)

**Fig.2.8.** Mechanism of glycolysis of PET waste

The ester group present in polyester macromolecule gets protonated in the presence of glacial acetic acid as shown in (Fig.2.8). This increases the polarity of the carbonyl group. In the glycolysis reaction, excess of ethylene glycol is used as a solvent.
The nucleophile ethylene glycol attacks the protonated carbonyl group of polyester and causes cleavage of the polymeric chain to get the monomer, BHET, as shown. When the salts of Li, Na, or K are used in place of glacial acetic acid, they are ionized, forming a complex with the carbonyl group of ester in PET. This complex facilitates the attack of ethylene glycol on PET, which in turn leads to the formation of BHET.

Good yields (>60%) of the monomer BHET were obtained using these chemicals as depolymerization catalysts. The qualitative and quantitative yields of the monomer obtained using these catalysts are most comparable with the conventionally used heavy metal catalysts such as zinc acetate and lead acetate. The chemicals used being cheap and comparatively less harmful to the environment, offered further advantages in chemical recycling of polyester waste fibres.

The glycolysis of PET bottle waste was carried out under atmospheric pressure in excess of EG (Shukla et al., 2008). Optimization of the parameters of glycolysis gave the yield of pure BHET of about 65%. The natural and environmentally safe large-pore aluminosilicates having considerably large void spaces such as β-zeolite and Y-zeolite were effectively used for the depolymerization of PET bottle waste with yield comparable to the conventional heavy metal catalysts like zinc acetate and lead acetate.

PET waste of various molecular weights (Mv ≈ 13500 and 18000) was glycolyzed under different conditions including varying the PET/EG proportion, temperature and time (Grzebieniak and Wesołowski, 2004). The glycolysis products, obtained under different conditions with different contents of oligomers (about 50 and 70%), were used as raw materials in the synthesis of degradable polyesters of ethylene terephthalate and L-lactic acid. These polymers obtained gave values above 65.Cm^3/g of the reduced viscosity, a melting temperature below 192°C and good melt stability at 260 °C.

Waste PET flakes were depolymerized by using EG, PG, DEG, and triethylene glycol (TEG) in the presence of zinc acetate as catalyst (Ozturk and Guclu, 2004). All glycolysis products were reacted with maleic anhydride and mixed with styrene monomer to get unsaturated polyester (UP) resins. The mechanical properties and curing behaviours of the waste PET based UP resins were comparable with the reference resins. The DEG- and TEG-based resins were more flexible than are PG-based resins due to the ether linkage. But, PG-based resins have higher tensile strength and hardness than do
DEG- and TEG-based resins. It appears that it is feasible to recycle waste PET as UP resins by glycolysis reactions using different glycol compounds and glycol compounds mixtures.

The monomer BHET was obtained with high purity and significant yield by depolymerization of waste PET (Sun et al., 2005). The glycolysis reaction was carried out at 196°C with a weight ratio of EG to PET from 0.5 to 6; weight ratio of catalyst to PET from 0 to 1.5% and time of 1-5 h in the presence of zinc acetate as a transesterification catalyst. The optimal conditions were found as reaction time of 3 h, weight ratio (EG to PET) of 5, weight ratio (catalyst to PET) of 1% and the yield of BHET was as high as 85.6%.

Useful coating products may be obtained by glycolysis of post-consumed PET wastes using poly (ethylene glycol) (PEG) of various molecular weights (200, 400, 600) (Patel et al., 2006). The depolymerized oligoesters obtained were transesterified with castor oil to obtain saturated hydroxyl-functional polyester polyols. Two-pack coating systems were formulated using these resins as base component and melamine formaldehyde resins as hardener component. The results obtained showed that the coating properties are influenced by the molecular weight of PEG and the amount of PET used for glycolysis.

Recycling of PET waste through glycolysis was successfully performed to obtain unsaturated polyester resin (Ahmed et al., 2007). This resin offered a function as matrix for natural filler in a rice husk (RH) reinforced thermoset. The incorporation of RH into polyester matrix increased the tensile modulus, hardness, and water absorption but decreased the tensile strength and elongation at break. With the alkali surface treatment, the properties of RH filled polyester, synthesized from glycolyzed product of PET waste, were improved significantly.

BHET obtained from glycolysis of PET waste was converted to different fatty amide derivatives to obtain quaternary ammonium compounds (Shukla et al., 2008). The products were characterized by infrared spectroscopy. Application of these synthesized compounds was carried out on cotton fabric; they were evaluated for performance and were found to give good results.
Products of the waste PET glycolysis were used as polyhydroxyl compounds in the reaction with epichlorohydrin to obtain new epoxy materials suitable for the modification of low molecular weight epoxy resins (Czub, 2008). Mechanical properties and thermal and chemical stability of the composites with epoxy resins based on glycolyzed PET wastes depend on the glycol type and contents of the oligomers in the degradation products. Long chain oligomers fragments built into the structure of cured epoxy composites provide better properties of cured materials than the modification only with the resin based on pure BHET monomer or resins based on waste PET glycolyzed with short chains glycols.

PET fibre waste was glycolytically depolymerized using excess of EG in the presence of sodium sulphate as catalyst (Shukla et al., 2009). The product, pure BHET was obtained with >60% yield by successive recrystallization. BHET was converted to bis(2-chloroethylene terephthalate), reacted with the p-nitro benzoic acid, reduced and then reacted with bromine and potassium thiocyanate to obtain benzothiazole derivative. Coupling with N,N-diethylaniline produced a bright yellow disperse dye (Dye A). Similarly, coupling of p-amino benzoic ester with N,N-diethylaniline led to an orange coloured disperse dye (Dye B). The application of these dyes on polyester fabric showed good colouration characteristics with satisfactory performance properties. Among the two synthesized dyes, Dye A gave a bright yellow colour whereas Dye B gave orange colour.

Recycling of PET waste was achieved through glycolysis using DEG and poly(ethyleneglycol) (PEG 400), which yielded different fractions that exhibited hydroxyl numbers of 174.41 and 54.86 mg of KOH/g, respectively (Essawy et al., 2012). The products of glycolysis from both cases were individually incorporated as modifiers during the synthesis of urea-formaldehyde resins from both the basic as well as acidic stages, respectively. The resin activation, revealed by gel time data, lead to the conclusion that these glycolysis fractions were involved effectively in the network structure of the resin which could further be confirmed by the improvement in adhesion strength in the dry state and their moisture resistance after immersion in water.

Removal of basic dyes (Safranine T and Brilliant Green) from aqueous media was carried out using depolymerization products (DP) obtained from aminoglycolysis of waste PET waste with diethylamine and EG (Acar et al., 2012). Adsorption of synthetic
dyes occurred by the electrostatic interactions of –COOH groups on DP samples and N group of the dyes. They also showed that Langmuir model was more suitable for basic dye adsorption onto DP samples, compared with Freundlich model.

Soft drinks PET bottles were depolymerized by glycolysis with different molar ratio of glycol, such as PG, triethylene glycol (TEG) and PEG 400, in the presence of zinc acetate catalyst (Cakic et al., 2012). The obtained glycolyzed products were reacted with isophorone diisocyanate (IPDI) and dimethylol propionic acid (DMPA), as potential ionic center for water dispersibility, and mixed with ethylene diamine (EDA) as extender chain to prepare polyurethane dispersions. The degradation profile of the dispersions was dependent on mole ratios of PET to glycol in glycolyzed products. The samples based on PET/glycol molar ratio 1:10 possess better thermal properties but less valued hardness coatings which can be ascribed to increased length of glycol in glycolyzed oligoester polyol. The samples based on lower mole ratio, PET/glycol(1:2) exhibit two distinct \( T_g \), which indicate that in these cases two kinds of hard segments are formed and not mixed at molecular level.

Imran et al. reported monophasic metal oxides (Mn\(_3\)O\(_4\), ZnO, and Co\(_3\)O\(_4\)) and mixed metal oxide spinels (ZnMn\(_2\)O\(_4\), CoMn\(_2\)O\(_4\), and ZnCo\(_2\)O\(_4\)) for application as transesterification catalysts in PET glycolysis (Imran et al., 2013). They reported mixed-oxide spinels exhibited better catalytic performance than the single metal oxides because the former had greater surface areas and higher acidic site concentrations on the catalyst surface. The maximum yield (92.2%) was obtained with tetragonal ZnMn\(_2\)O\(_4\) spinel catalyst at 260 °C, 5 atm, 1.0 wt% (catalyst/PET), 17.2 (EG/PET molar ratio), and 60 min reaction time. This high yield is attributed to many factors (surface area, acidity), as well as the presence of Jahn–Teller interactions of Mn\(^{3+}\) in the Zn\(^{2+}/\)Mn\(^{3+}\) cation pair of the tetragonal ZnMn\(_2\)O\(_4\) spinel. The mild reaction conditions pushed the equilibrium yield to above 90% (whereas most literature reports are approximately 70%) and demonstrated the potential of the developed catalysts and process.

**Glycolysis of PET waste using ionic liquids**

PET waste was depolymerized using EG in the presence of ionic liquid as catalyst (Wang et al., 2009). They found that the purification process of the products in the
glycolysis catalyzed by ionic liquids was simpler than that catalyzed by traditional compounds, such as metal acetate. They illustrated the effects of reaction parameters, such as the amount of catalyst, glycolysis time, reaction temperature, and water content in ionic liquid on the conversion of PET, selectivity of BHET, and distribution of the products. The results showed that the conversion of PET increases with increasing amount of catalyst, glycolysis time, and reaction temperature, but decreases with the addition of water in \([\text{Bmim}]\text{Cl}\).

The glycolysis of PET was studied using several ionic liquids and basic ionic liquids as catalysts (Yue et al., 2011). The basic ionic liquid, 1-butyl-3-methylimidazolium hydroxyl ([Bmim]OH), exhibited higher catalytic activity for the glycolysis of PET, compared with 1-butyl-3-methylimidazolium bicarbonate ([Bmim]HCO₃), 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) and 1-butyl-3-methylimidazolium bromide ([Bmim]Br). A great increase in PET conversion and BHET yield was observed when the reaction temperature increased from 150 °C to 190 °C. Results show that reaction temperature is a critical factor in this process. Under the optimum conditions of m(PET):m(EG): 1:10, dosage of [Bmim]OH at 0.1 g (5 wt%), reaction temperature 190 °C and time 2 h, the conversion of PET and the yield of BHET were 100% and 71.2%, respectively.

The depolymerization of PET in ethylene glycol was catalyzed by imidazolium-based Fe-containing ionic liquid, 1-butyl-3-methylimidazolium tetrachloroferrate ([bmim]-FeCl₄) (Zhang et al., 2010). This magnetic ionic liquid exhibited higher catalytic activity for the glycolysis of PET, compared with FeCl₃ or ionic liquid, 1-butyl-3-methylimidazolium chloride ([bmim]Cl). They also reported that the onset reaction temperature of the glycolysis process catalyzed by [bmim]-FeCl₄ is much lower, being 140 °C. They proposed a mechanism, which indicated that the high catalytic activity of [bmim]-FeCl₄ was attributed to the synergic effect of its cation and anion that makes the attack of oxygen in EG on the carbon cation of the ester group much easier.

### 2.1.4. Aminolysis

Aminolysis is any chemical reaction in which a molecule is split into two parts by reacting with a molecule of an amine (Fig.2.9). The example may be reaction of a
primary amine or secondary amine with a carboxylic acid or with a carboxylic acid derivative to form an amide. The carboxylic acid derivatives can be esters, anhydrides, acid halides or any other activated species.

![Diagram of PET waste aminolysis](image)

**Fig.2.9.** Aminolysis of PET waste

Aminolysis of PET waste is the reaction of PET with different aqueous amine solutions to yield the corresponding diamides of TPA and EG. The reaction was usually carried out using primary amine aqueous solutions, most frequently methylamine (Awodi et al., 1987; Popoola, 1988; Collins et al., 1991), ethylamine (Collins et al., 1991), and ethanolamine (Collins et al., 1991) in the temperature range of 20-100 °C. Anhydrous n-butylamine was also applied as an aminolytic agent at a temperature of 21 °C (Collins et al., 1991). Most of these investigations have been focused on selective PET degradation by an aqueous solution of methylamine so as to determine its morphology.

PET in the form of waste fibres and disposable soft drink bottles was subjected to depolymerisation through aminolysis using excess of ethanolamine in the presence of different simple chemicals, namely glacial acetic acid, sodium acetate and potassium...
sulphate, as catalysts (Shukla & Harad., 2006). The product bis(2-hydroxy ethylene)terephthalamide (BHETA) obtained was in its pure form with sufficiently high yields with all the catalysts. The maximum yields of BHETA under optimized conditions were 91.1% from PET fibrous waste and 83.2% from bottle waste. In the absence of any catalyst, the yield was only 52%. This difference in the yields was attributed to the molecular weight and its distribution in PET fibrous waste and the bottle waste. For the fibre grade PET, the molecular weight is lower and the molecular weight distribution is narrower than that for the bottle grade PET in order to attain higher viscosity for the latter, necessary for the blow-molding process.

Shamsi et al. reported the use of BHETA obtained from aminolysis of PET waste (Shamsi et al., 2009). Novel polyurethanes were then synthesized, based on BHETA, 1,4- butanediol (BD), ether-type polyol and various molar ratios of hexamethylene diisocyanate (HMDI). They showed that BHETA participates in the chemical structure of synthesized polyurethanes based on BHETA, HMDI, Polyol and BD.

The degradation of PET waste by making use of hydrazine monohydrate was investigated at ambient temperature and pressure (Soni et al., 2009). The end product was characterized as terephthalic dihydrazide (TPHD) and further used in PVC compounding as secondary plasticizer. The hardness, tensile strength, elongation at break, thermal stability, and compatibility of the PVC sheet were studied. They found that the hardness of PVC sheets decrease with increase in the amount TPHD and thermal stability of the PVC sheets increased with increasing amount of TPHD. The thermal stability of PVC sheets was improved by 5–15%.

BHETA obtained from chemical recycling of PET waste was used for synthesis of various bio degradable polyurethanes based on polycaprolactone diol (Sadeghi et al., 2011). At first, polyols with different molecular weights were synthesized through ring opening polymerization of caprolactone by BHETA, and then urethane linkages were formed using HMDI without chain extender. They showed excellent chemical, thermal and mechanical properties.

PET postconsumer bottle waste was cut to very small size and then subjected to a aminolysis process with ethanol amine as a degradative agent in the presence of a catalyst, dibutyl tin oxide, sodium acetate and cetyltrimethyl ammonium bromide
The reaction was performed in sunlight: a beneficial, clean, cheap, and renewable source of energy to obtain the BHETA. Then, the end product obtained (i.e., BHETA) showed promising results as anticorrosive ingredients in corrosion-protective paints.

Bis(2-aminoethyl) terephthalamide (BAET, or trimer) and α,ω-aminoligo(ethylene terephthalamide) (AOET, or oligomers) were obtained from the reaction of PET waste with excess amount of ethylenediamine (EDA) (Hoang & Dang, 2013). The aminolysis of PET waste by using excess of EDA produces not only trimer BAET, but other higher molecular weight oligomers AOET. The maximum yield of trimer BAET was only 75% when input molar ratio of EDA:PET more than 14:1 was used. The amino end caped trimer BAET and oligomers AOET, could be used to prepare new polyamides, polyimides.

**Aminolysis of PET waste using ionic liquids**

Aminolytic depolymerization of PET bottle waste with ethanolamine and hydrazine hydrate under atmospheric conditions was investigated in the presence of room temperature ionic liquids (Shukla et al., 2012). 1-hexyl-3-methylimidazolium trifluoromethanesulfonate (Hmim.TfO) and 1-butyl-3-methylimidazolium hydrogen sulfate (Bmim.HSO₄). (Hmim.TfO) were found to be the most efficient catalysts to obtain high yields of the aminolysis products BHETA and TPHD using ethanolamine and hydrazine hydrate, respectively.

**2.1.5. Ammonolysis**

Ammonolysis is the reaction of ammonia with PET to produce a terephthaldiamide (Fig.2.11). This can be converted to terephthalonitrile, and further, to other chemical substances.

Very good results were obtained from the ammonolysis of PET waste from postconsumer bottles; the process was carried out under a pressure of about 2 MPa in a temperature range of 120-180 °C for 1-7 h. After the reaction was completed, the amide produced was filtered, rinsed with water, and dried at a temperature of 80 °C. The
product has a purity of not less than 99%, and the yield was above 90% (Blackmon et al., 1988).

Fig. 2.11. Ammonolysis of PET waste

Soni & Jain spectroscopically investigated the end products obtained from ammonolysis of PET waste using zinc acetate as catalyst (Soni & Jain, 2007). The products obtained by ammonolysis in the presence and absence of catalyst were separated and characterized by spectroscopic techniques namely FTIR and Mass Spectrometry (MS) together with Scanning Electron Microscopy (SEM) and Differential Thermal Analysis (DTA). The end products were characterized as 1, 4-benzene dicarboxamide in both the cases and were found to be same throughout the course of reaction. The results showed that the catalyst reduces the time of completion of reaction from 45 to 15 days.

2.2. Chemical recycling of PET waste using microwave irradiation

Microwaves are radio waves with wavelengths ranging from as long as one meter to as short as one millimeter, or equivalently, with frequencies between 300 MHz
(0.3 GHz) and 300 GHz. A microwave oven passes (non-ionizing) microwave radiation (at a frequency near 2.45 GHz) through food, causing dielectric heating primarily by absorption of the energy in water. Water in the liquid state possesses many molecular interactions that broaden the absorption peak. In the vapour phase, isolated water molecules absorb at around 22 GHz, almost ten times the frequency of the microwave oven. Microwave heating is used in industrial processes for drying and curing products.

Since mid-1990s, the number of publications has increased significantly on microwave assisted organic reactions. The main reasons for this increase include the availability of commercial microwave intended for organic chemistry and development of solvent free techniques, which has improved the safety aspects, but are mostly due to an increase interest in shorter reaction times.

<table>
<thead>
<tr>
<th>MICROWAVE HEATING</th>
<th>CONVENTIONAL HEATING</th>
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<tbody>
<tr>
<td>Energetic coupling</td>
<td>Conduction/ convection</td>
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<tr>
<td>Coupling at the molecular level</td>
<td>Superficial heating</td>
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<tr>
<td>Rapid</td>
<td>Slow</td>
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<tr>
<td>Volumetric</td>
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<tr>
<td>Selective</td>
<td>Non-selective</td>
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<tr>
<td>Dependant on materials</td>
<td>Less dependent on materials</td>
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Table 2.1. The basic characteristics of microwave and conventional heating

The microwave radiation passes through walls of vessel and heats only reactant and solvent, not the reaction vessel itself. If the apparatus is properly designed, the temperature increase will be uniform throughout the sample, which can lead to formation of less byproduct and/or decomposition products.

As with all electromagnetic radiations, the microwave radiation is divided into electric field component and magnetic field component. The former component is responsible for the dielectric heating, which is effected via two mechanisms.
**Dipolar polarization mechanism**

If a dipole is exposed to an electric field, it normally aligns itself with the field to minimize the free energy. The time taken for this alignment (known as the response time) is dependant on the frequency of the field and the strength of the dipole. Considering the frequency dependency of the response time, three scenarios are possible. At low frequencies, the time taken by the electric field to change direction is larger than the response time for the dipoles; hence the dipoles remain aligned with the electric field. At high frequencies the electric field changes direction much faster than the response time of the dipoles, hence the dipoles are unable to rotate and they remain static. However, in the microwave range of frequencies the time required by the field to change the direction is of the same magnitude as the response time of the dipoles. The dipoles experience torque that causes them to rotate as they try to orient themselves with the field, but the resulting polarization of the molecule lags behind the changes of the field. As the dipoles are not perfectly aligned with the field, they are not in the lowest energy state, hence an energy transfer must be occurring. The lag indicates that the molecule absorbs energy from the electromagnetic field and is being heated.

**Conduction mechanism**

This mechanism of energy transfer from microwaves to a sample requires the presence of ions or ionic species in the sample. The electric field of the microwaves generates ionic motion as the ions try to realign themselves to the rapidly changing field, resulting in rapid superheating. Ionic conduction is sensitive to temperature; as the temperature increases, the transfer of energy becomes more efficient. Alumina, for example, has a conductivity that rises with temperature, as the number of electrons thermally excited into the conduction band increases.

**Recycling of PET waste**

Recycling of PET was examined using hydrolytic depolymerization in an alkaline solution under microwave irradiation (Achilias et al., 2010). The reaction was carried out in a sealed microwave reactor in which the pressure and temperature were controlled and recorded. The main products were the monomers TPA and EG. Microwave irradiation
was found to reduce the time needed to achieve a specific degradation of PET significantly, with almost complete depolymerization occurring in 30 min at 180 °C and only 46W of microwave power. Using a phase transfer catalyst (TOMAB) resulted in the same amount of unreacted PET but at significantly lower depolymerization temperatures. PET depolymerization is favoured by increasing temperature, time and alkaline solution concentration, while it is not influenced much by the amount of catalyst used.

Microwave-assisted hydroglycolysis of PET using an excess of methanol, ethanol, 1-butanol, 1-pentanol, and 1-hexanol in the presence of different simple basic catalysts, namely, potassium hydroxide, sodium hydroxide, sodium acetate, and zinc acetate, is reported (Nikje & Nazari., 2006). Reactions were performed at short times without any side reactions. The products TPA and EG were obtained in their pure form with sufficiently high yields with potassium hydroxide.

Glycolysis of PET bottle waste was carried out using microwave energy. A domestic microwave oven of 800W was used with suitable modification for carrying out the reaction under reflux (Shukla & Pingle., 2008). The catalysts used for the depolymerization in EG were zinc acetate and some simple laboratory chemicals such as sodium carbonate, sodium bicarbonate and barium hydroxide. They observed that under identical conditions of catalyst concentration and PET:EG ratio, the yield of BHET was nearly same as that obtained earlier by conventional electric heating. However, the time taken for completion of reaction was reduced drastically from 8 h to 35 min.

Recycling of waste PET bottles was examined using glycolytic depolymerization with diethylene glycol, under microwave irradiation (Achilias et al., 2010). The reaction was carried out in a sealed microwave reactor in which the pressure and temperature were controlled. Complete depolymerization was observed at irradiation powers greater than 150 W for 2 min, or 100 W for 5 min.

PET disposable soft drink bottle waste was subjected to depolymerization via aminolysis using excess of ethanolamine (Shukla and Pingle, 2009). The reaction was carried out under non conventional microwave energy in the presence of different simple chemicals as catalysts namely, sodium acetate, sodium bicarbonate and sodium sulphate. High yields of BHETA (>90%) at very low reaction time (4 min) was obtained with common and cheap chemicals as catalysts.
Aminolytic depolymerization of PET with ethanolamine under microwave irradiation and without the use of any catalyst was investigated (Achilias et al., 2010). In the experiments carried out under constant microwave power, complete depolymerization was observed at irradiation powers greater than 100W for a time less than 5 min. In general, PET depolymerization and recovery of the main product, BHETA, were favoured by increasing temperature, time and microwave power.

2.3. Chemistry of Bis-oxazolines and bis-oxazines

Oxazolines are 5 membered heterocyclic compounds while, oxazines are 6-membered heterocyclic compounds. They have been used as chain extenders in polyester and nylon composites and cross-linking agents in powder paint compositions.

Bayer filed a patent in 1973 at Germany for the process for production of oxazoline derivatives (Deiter and Hermann, 1974). They reported the synthesis of bis oxazoline by introducing corresponding terephthalamide derivatives to a mixture of 85% phosphoric acid and sulphur trioxide to obtain yield around 90%.

Moghadam et al. demonstrated that highly sulphonated carbon solid acids can be used as a green and reusable catalyst for efficient synthesis of oxazolines and bis-oxazolines under heterogeneous conditions from nitriles and alkanol amines (Moghadam et al., 2009). They also exposed this system to ultrasonics irradiation which enhanced the catalytic activity of the carbonbased solid acid and led to higher product yields and shorter reaction times.

Benicewicz et al. reported the synthesis of oxazoline and oxazine compounds by ring closure reaction of precursor’s β-halo amides or γ-halo amides respectively (Benicewicz et al., 1995). These amide intermediates were prepared from reaction of acid chloride or anhydride with 2-chloro ethylamine (for oxazoline) and 3-chloro propylamine (for oxazine). The ring closure of amide precursors to oxazoline and oxazine products was accomplished by using basic reagent such as fluoride salt (Potassium fluoride) supported on an inorganic substrate.

Bis-oxazoline has also been reported to be prepared from carboxylic esters and amino alcohols using lanthanide(III)chloride as catalyst with n-butyl lithium in toluene (Natale et al., 1997). The product yield obtained was in the range of 44-50%.
New polythioetherimides with amide linkages were prepared by polyaddition reaction of 2,2’-(1,4-phenylene)-bis(2-oxazoline) (PBO) with bis(2-mercaptoethyl)ether and various bismaleimides and biscitraconimides (Gaina, 2006). The polymers were obtained in 86-92 % yields and their inherent viscosities ranged between 0.212-0.387 dL/g. Flexible films for the polymers were obtained by casting from DMF solutions. Their thermal behaviour was monitored by DSC and TGA measurements and showed glass transition temperature range between 150 °C and 200 °C.

Ven benthem et al., invented the process for the preparation of powder paint composition comprising functional polyester, bis-oxazoline as crosslinker, titanium oxide, benzoin and weight flow agent (Ven benthem et al., 2002). The composition was used in powder coatings for use on metal, wood or plastic substrates.

Kim et al. prepared melt blends of polyamide 6 (PA 6) and polyester elastomer (PEL) in corotating twin screw extruder using bis-oxazoline as coupling agent (CA) (Kim et al., 1999). They observed that the notched impact strength of PAL as well as PA 6/ PEL blends increased with the addition of CA. They also investigated the viscosities of base resins as well as blends, which was found to increase with addition of CA.

Bis-oxazine and bis-oxazoline have been recently reported to be synthesized from aromatic dinitrile with corresponding alkanol amines using Zinc-2-ethyl hexanoate at 140 °C for 6 h (Kuebelbaieck et al., 2010). After the reaction ended, excess alkanol amine was removed by distillation process under vacuum, to obtain good product yield around 75 % with high purity (>99 %).

2.4. Ionic liquid catalyzed synthesis of oxazoline

Ionic liquids (ILs) have attracted increasing interest recently in the context of green organic synthesis. Although ionic liquids were initially introduced as alternative green reaction media because of their unique chemical and physical properties, today they have marched far beyond this boundary, showing their significant role in controlling reactions as solvent or catalysts. Another feature of ionic liquids is their ability to be reused many times.

‘Ionic liquid’ is now the commonly accepted term for low-melting salts (melting-point typically <100 °C) obtained by the combination of large organic cations with a
variety of anions (Fig. 2.12). Although estimates vary, there is no doubt that the number of combinations of anions and cations that can give rise to potential ILs is vast. If low melting salts are liquid at room temperature, then they are termed as ‘Room Temperature Ionic Liquids’ (RTILs).

Advantages of ILS

- Easy separation
- Very low vapour pressure
- Non-flammable substance
- High thermally stable
- Wide liquid regions
- Favourable solvating properties
- Often termed as “Designer solvents”

Recently, sulphonic acid group functionalized imidazole based ‘Bronsted acidic ionic liquids’ (BAILs) have been reported to carry out various organic reactions.

Davis et al. reported the first ILs that were designed to be strong bronsted acids. In each of the new IL, an alkane sulphonic acid group is covalently tethered to the IL cation (Davis et al., 2002). Reaction of the neutral nucleophiles N-butyl imidazole or triphenylphosphine with 1,4-butane- or 1,3-propane sultone, respectively, produced the
requisite zwitterions in excellent yields. In the second step, the simultaneous realization of the latent acidity of the zwitterions and their conversion into ionic liquids (converting sulphonate group into alkane sulphonic acid) was accomplished. The chemical yields for both the zwitterion formation and acidification steps were quantitative. Moreover, since neither reaction produced byproducts, the IL syntheses are 100% atom efficient. Both new IL were screened as solvent/catalysts for several classical acid-promoted organic reactions, namely Fischer esterification, alcohol dehydrodimerization and the pinacol/benzopinacole rearrangement. Both new ionic liquids proved catalytically active in these reactions.

An efficient route to prepare ionic liquids with chloroalkylsulphonate anions was reported; the synthesis proceeded in a one-step ring-opening reaction of sultones with an organic chloride salt and provided a very attractive access to new anion functionalized ionic liquids (Pappe et al., 2008). The resulting chloro alkyl sulphonates exhibited a number of interesting physico-chemical properties but their thermal stability was limited to a practical application range below 150 °C.

Xian et al. reported the synthesis of biodiesel using BAILs N-methyl-2-pyrrolidonium methyl sulphonate ([NMP][CH3SO3]) as a catalyst, specially with free long-chain fatty acids or their mixtures, as well as with low-molecular weight alcohols as substrates (Xian et al., 2009). This catalyst showed good catalytic and reusable performance under mild conditions and without any additional organic solvent. The ionic liquid was reused eight times after the water in the ionic liquid was removed.

Sulphonic acid group functionalized imidazole based BAILs were synthesized and their activities were investigated in the hydration reaction of alkynes (Kore & Srivastava, 2012). N-SO3H functionalized BAIL ([SO3Hmim][Cl]) was found to be more active than the N-R-SO3H (R = alkyl/benzyl) functionalized BAILs. These reactions were easy to perform and the purification protocol was simple.

Oxazolines are five-membered heterocyclic compounds having one double bond. The double bond may be located in one of three positions, therefore making possible the existence of three different oxazoline rings. The 2-oxazoline structure is the most common, with 3-oxazolines and 4-oxazolines existing primarily as laboratory research compounds.
The oxazoline ring presents an interesting structure on which to build a wide variety of compounds having properties which make them of interest in many fields of application. Hydrogens located on the α carbon of an alkyl group in the 2 position are active and are readily replaced with other groups. In addition, the 2-oxazoline ring has two sites in the 4 position and two in the 5 position where reactive groups may be located. Also, the nitrogen of the oxazoline is basic and forms salts with acids and quaternary compounds with alkyl halides.

2-oxazolines are widely found in natural products of a different range of biological activities (Miller, 1992) in catalysis (Hargaden, 2009) and as synthetic intermediates (Braga, 2008). 2-oxazolines are important functional in organic chemistry as their hydrolyzable property makes them precursors of carboxylic acids in pharmacology. Also Bis-oxazolines and different chiral oxazolines have been widely used as auxillaries and ligands in asymmetric synthesis (Fig.2.13).

Due to wide applications of 2-oxazolines, numerous synthetic methodologies have been developed over the years. Reaction of amino alcohols with carboxylic acids using high temperatures up to 200-220 °C and long reaction times (12-18 h) (Frump, 1971) and with nitriles using lewis acid at high temperatures with elimination of ammonia (Bolm, 1991).
Kamata & Agata, carried out reaction of carboxylic acid with amino alcohols using commercially available orthoesters with 1, 2-dichloroethane as solvent to prepare oxazoline (Kamata and Agata, 1998). They also investigated the optical purity of products and found comparable results to those reported in literature.

Oussaid et al. reported the preparation of 2-oxazolines under microwave irradiation by two different ways (Oussaid et al., 1995). In a first one, imino ether hydrochlorides were reacted with amino alcohols in the presence of alumina supported potassium fluoride, in an open vessel while, in second one, amino alcohols were directly reacted with imino ethers in a closed vessel to get very good yields of corresponding 2-oxazolines.

Katrizky et al. carried out microwave reactions of 2-amino-2-methyl-1-propanol or 2-aminoethanethiol hydrochloridewith readily available N-acylbenzotriazoles in the presence of SOCl₂ to produce 2-substituted-2-oxazolines in 84-98% yields and 2-substituted thiazolines in 85-97% yields, respectively (Katrizky et al., 2004). These results demonstrated a new application of N-acylbenzotriazoles in the preparation of oxazolines and thiazolines under mild conditions and short reaction times with microwave irradiation.

A popular approach to prepare oxazolines involves the intramolecular cyclization of β-hydroxy amide, through activation of –OH group as a leaving group. Various dehydrating agents have been reported for cyclization of different hydroxy amides.

Phillips et al. presented the combined results of studies into the use of diethylaminosulphur trifluoride (DAST) or bis (2-methoxyethyl)aminosulphur trifluoride (Deoxo-Fluor) for the cyclodehydrative conversion of β-hydroxy amides to oxazolines at low temperature, along with a one-pot procedure for the synthesis of oxazoles from β-hydroxy amides (Phillips et al., 2000). Results indicated that DAST and Deoxo-Fluor were compatible with a wide range of functional groups and that these reagents perform comparably in terms of yields for the cyclization of serinederived peptidyl β-hydroxy amides.

A mild and highly efficient one pot–one step condensation and/or condensation–cyclization of various acids to amides and/or oxazolines using Deoxo-Fluor reagents are
described (Kangani and Kelley, 2005). Parallel syntheses of various free fatty acids with 2-amino-2,2-dimethyl-1-propanol resulted with excellent yields.

β-hydroxyamides was reported to be cyclized by reaction with diisopropyl-carbodiimide (DIC) to give the corresponding 2-oxazolines in high yields (Linclau et al., 2004). It was shown that the cyclization proceeded in good to excellent yields after 5h reflux in 1,4-dioxane, and in merely 5min under microwave irradiation (150 °C).

Not much work is reported for the synthesis of 2-oxazolines using ILs. There is only one report in which author described synthetic approach to obtain 2-oxazolines using ILs. This method combined amide bond formation from acids and amino alcohols and cyclic dehydration in a one-pot synthesis (Kamakshi et al., 2006). The protocol afforded good yields of substituted 2-oxazolines (85 %) in indium chloride/ionic liquid media ([BMIM][Cl]), as shown in Fig.2.14. The ionic liquid was used in a molar ratio of 1:7 (reactant/IL). When the reaction was performed without the presence of an ionic liquid, in chlorobenzene under reflux conditions (3 h) with InCl₃ as a catalyst, the product yield was only 50%.

![Fig.2.14](image.png)

**Fig.2.14.** Synthesis of 2-oxazoline using IL from carboxylic Acids and aminoalcohols

### 2.5. Synthesis of bis-heterocyclic compounds from PET waste

A heterocyclic compound is an organic compound in which one or more of the carbon atoms in the backbone of the molecule has been replaced by an atom other than carbon. Typical hetero atoms include nitrogen, oxygen, and sulfur. The heterocycles are enjoying their importance as being the center of activity. The nitrogen containing heterocycles are found in abundance in most of the medicinal compounds.
1,2, 4-Triazole derivatives

The presence of three nitrogen hetero-atoms in five-membered ringsystems defines an interesting class of compounds, the triazole. This may be of two types, the 1,2,3-triazoles (1) and the 1,2,4-triazoles (2) (Fig.2.15).

Fig.2.16. Biological activities of triazole derivatives

Triazoles have been found to possess various biological activities such as anti-fungal, anti-inflammatory etc (Fig.2.16).
Substituted-1,2,4-triazole-3-thiones (C) have been prepared in one stage from the reaction of acid hydrazide (A) with alkyl or aryl isothiocyanate in the presence of a KOH to undergo cyclization reaction (Fig. 2.17). The alternative method used to synthesize compound, wherein acid dihydrazide reacted with carbon disulphide and KOH solution forms salt (D) which undergoes cyclization in presence of acidic solution (Patani and LaVoie, 1996; Lima and Barreiro, 2005).

1, 3, 4-Thiadiazole derivatives

In last decade, attention has been increasingly paid to the synthesis of bis heterocyclic compounds, which exhibit various biological activities (Holla et al., 2002; Semenov et al., 2001; Moskvin et al., 2001).

Shaker et al., reported the synthesis of 1,4-bridged bis-1,2,4-triazoles and bis-1,3,4-thiadiazoles by reacting terephthalic acid dihydrazide (TPHD) with phenyl/benzyl isothiocyanate (Fig. 2.18). Bis-oxadiazoles derivatives obtained by reacting TPHD with phenyl isocyanate. The reported compounds were tested for antibacterial and fungicidal activity and found to possess moderate to good activity (Shaker et al., 2005).
Fig.2.18. Synthesis of bis-heterocyclic compounds

Earlier, in our laboratory, the product (terephthalic dihydrazide) obtained from aminolytic depolymerization of PET using hydrazine hydrate has been converted into various useful chemicals such as textile dyes and some of them were found to possess even antibacterial activity (Shukla et al., 2009, 2010). They have reported the synthesis of novel series of 1,4-bis(6-(substituted phenyl)-[1,2,4]-triazolo[3,4-b]-1,3,4-thiadiazoles and 4-bis(substituted phenyl)-4-thiazolidinone derivatives from terephthalic dihydrazide which is being obtained from PET waste. Bis-oxadiazole and bis-hydrazone derivatives
have also been reported. Most of the reported compound showed moderate antibacterial activity compared to commercial compounds.

2.6. Copper catalyzed Sonogashira coupling reaction

The palladium catalyzed C–C bond formation process, which is able to couple a terminal sp hybridized carbon from an alkyne with a sp² carbon of an aryl or vinyl halide (or triflate) is commonly termed as a Sonogashira coupling (Fig.2.19). The reaction name arises from the discovery in 1975 by Sonogashira, Tohda, and Hagihara that this process could be performed easily at room temperature using a palladium source such as PdCl₂(PPh₃)₂ as catalyst, combined with a co-catalyst CuI in small amounts in an amine as solvent. This reaction is widely used for the synthesis of a variety of intermediates in pharmaceuticals, agrochemicals and natural products (Chinchilla and Najera, 2007 & 2011)

![Fig.2.19. General reaction scheme of sonogashira coupling reaction](image)

The copper-cocatalyzed sonogashira reaction is believed to take place through two independent catalytic cycles as shown in Fig.2.20, where a tertiary amine is represented as base, with other amines or inorganic bases performing similarly. The generally accepted catalytic cycle for the palladium catalyst (Pd-cycle) is based on a usually fast oxidative addition of R¹-X (R¹= aryl, hetaryl, vinyl; X = I, Br, Cl, OTf) to the real catalyst generated from the initial palladium complex.
This is classically thought to be 14-electron Pd$^0$L$_2$, formed by reduction of different palladium (II) complexes under the employed reaction conditions, as it is known that n-electron donors, such as phosphanes, amines, and ethers, used as ligands and solvents, can reduce palladium(II) species typically via $\sigma$-complexation-dehydropalladation-reductive elimination. In the oxidative addition step, the characteristics of the R$_1$-X substrate are crucial, with this step being facilitated if X = I or OTf and if the electronic density is reduced on the C-X bond by the presence of electron-withdrawing groups. The next step in the Pd-cycle would connect with the cycle of the
copper co-catalyst (the Cu cycle). Thus, a usually rate determining transmetallation from the copper acetylide formed in the Cue cycle would generate a $^{1}\text{Pd}(-\text{CCR}^2)\text{L}_2$ species, which gives the final coupled alkyne after trans/cis isomerization and reductive elimination with regeneration of the catalyst.

The advent of this palladium/copper catalyzed method has greatly improved the reaction conditions and functional group tolerance and is currently the method of choice for the synthesis of a variety of diarylacetylenes. Most of the catalytic systems contain expensive palladium, which may become an important issue in large scale applications. Therefore, development of cheap metal catalyst for this type of coupling reactions is needed.

Research on the use of copper based catalyst is gaining much importance in recent years. Classic Ullmann reaction and Castro Stevens coupling were catalyzed by copper for the formation of these carbon-carbon and carbon-heteroatom bonds. These reactions suffer from certain drawbacks, which include high copper catalyst loading, high reaction temperature and irreproducibility of the reaction. Even if some of the limitations of copper catalyzed reaction can be addressed, then it may provide economically feasible alternative route for the use of expensive palladium catalyst.

A copper salt with different types of ligands has been used to catalyze Sonogashira reaction. Miura and coworkers demonstrated the first copper catalyzed coupling of a limited range of aryl and vinyl iodides with acetylenes using copper iodide and triphenylphosphine in presence of potassium carbonate as base to obtain unsymmetrical acetylenes in good yields (Miura et al., 1992). They also used DMF and DMSO as solvents and found that DMSO was effective for the reaction of aliphatic terminal alkynes. Miura’s work demonstrated that copper alone can catalyze the cross-coupling of acetylenes and aryl iodides.

Cross-coupling of aryl iodides with terminal alkynes catalyzed by a simple and inexpensive catalyst system of CuI/PPh$_3$ in water as the sole solvent has been reported (Liu et al., 2009). In the presence of CuI/PPh$_3$, with KOH used as a base, a number of aryl iodides were treated with alkynes to afford the corresponding products in moderate to excellent yields.
CuI/PPh₃-catalyzed coupling reaction of aryl iodides with terminal alkynes in neat water, carried out under microwave irradiation at 120 °C or refluxing using conventional heating, to produce the coupling products in excellent yields (Chen et al., 2007). They have used PPh₃ and TBAB as additives to improve the reaction parameters.

The phosphine ligands for copper catalyzed reaction have been replaced with other ligands such as amines. Sekar & Thakur developed an efficient, experimentally simple, and economically attractive DBU–CuBr complex catalyzed C-arylation of terminal alkynes with aryl iodides through a C_aryl–C_alkynyl bond forming reaction (Sekar and Thakur, 2009). Aryl iodides containing both electron-releasing as well as electron-withdrawing groups react with terminal alkynes to provide arylated alkyne products in high isolated yields.

In the presence of TBAB, CuI-catalyzed Sonogashira cross-coupling of variety of aryl halides and vinyl halides with terminal alkynes was conducted smoothly to afford the corresponding diarylacetylenes in moderate to good yields using DABCO (1,4-diazabicyclo[2.2.2]octane) as the ligand (Li et al., 2007).

A simple Cu(OAc)₂-catalyzed Sonogashira coupling reaction of a variety of aryl halides with terminal alkynes was conducted smoothly at 150 °C to afford the corresponding desired products in moderate to excellent yields with triethylamine as a solvent (Li et al., 2007). The also observed that, no oxidative homocoupling product was obtained using current optimized parameters.

Monnier et al. reported copper based efficient catalytic system for C-C coupling reaction (Monnier et al., 2008). They have carried out reaction using Cu(acac)₂/ β-diketone catalyst in DMF at 90-120 °C using K₂CO₃ as an inexpensive base. They have applied this significantly less expensive catalytic system than Pd-Cu catalyzed system to a wide range of variously substituted aryl iodides for coupling to both alkyl- and aryl-substituted terminal alkynes.

Copper (II) oxide and Cu metal, highly dispersed on inert oxides (silica, alumina), have been employed as pre-catalysts in ligand-free, palladium-free Sonogashira coupling reactions (Biffis et al., 2007). They obtained very good results with highly dispersed Cu metal on alumina, which exhibited high reactivity with aryl iodides. Electron-rich alkynes, in particular arylacetylenes, act as the most effective alkyne substrates. The use
of a readily available non-noble metal catalyst and the absence of ligands, allowed a simpler product recovery.

Yuan et al. developed an experimentally simple and general procedure for the Sonogashira coupling reaction of terminal alkynes with aryl halides in dimethyl sulphoxide catalyzed by nano-CuO in excellent and high yields (Yuan et al., 2011). Except for the solvent dimethyl sulphoxide and catalytic amount of nano-CuO, no other ligands or cocatalysts were required for the reaction to proceed.