LONG LASTING TECHNOLOGY FOR PET RECYCLING

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Abstract

This paper presents an original technology of transforming PET waste into the original raw materials and then of introducing them again into a PET processing cycle. The method used is the oxidizing-catalytic one of breaking the ester connections and releasing the terephthalic acid. The oxidizing mixture is formed of 95% nitric acid of 63-65% concentration, 5% hydrochloric acid of 37%, 0.01 % ammonium metavanadate and 0.05% copper chloride as compared to the oxidizing mixture. The reaction takes place in 2 phases: in the first phase, the PET waste are broken up, weighed, and inserted into a vessel and then melted at temperatures of 230-250^{0}C, until you obtain a fluid solution. Over the oxidizing mixture, the polymer melting was added, previously heated at 80-90ºC. Suddenly, it takes place a violent reaction with massive release of nitrogen, forming a solid, spongy mass, containing the glycolic monoester of the terephtalic acid resulted after the breaking of the ester connection from the polymeric chain. In the second phase, the reaction mixture was separated, the solid mass was transferred into a vessel to be broken up until becoming powder. This powder was introduced into a reaction balloon and the oxidizing mixture was poured over. The proof was stirred for 30 minutes, at 110-120ºC, after which it was cold, screened and washed several times with distilled water, until the complete removal of the oxidizing mixture and then dried for 3 hours at 120ºC. The FT IR spectrometrical analysis shows that the product obtained after the oxidation reaction is the terephtalic acid.

Key words: offals, PET, terephtalic acid, recycling.

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Introduction

The synthetic polymer production polyester type has been developed in the last 50 years, when a series of countries from Europe and Asia have extended the polyester production thanks to its involvement in all the economic branches (Becker and Berger, 1982). The largest part of the polyester production is used for the manufacturing of electronic household appliances, for wrapping food and beverage, and also for the pipe manufacturing for culture sewerage and irrigation. In the textile industry, polyesters are used for the manufacturing of the polyester threads which, combined to wool, cotton and flax are used to obtain cloths and knitted goods. Besides all the positive uses they have, there is also a great inconvenience, that is, they are not biodegradable. A PET bottle may be buried for years without getting decayed. Besides this inconvenience, there is another one, as important as this one, namely to keep the smells coming from various essences used for the manufacturing of juices and beverage for a long time, which makes them impossible to be used again.

Generally speaking, all the PETs can be used only once and they are considered to be major polluting agents for the environment. This is why in Romania PETs invade the entire environment: water, lakes, woods and so on.

To be recycled, these offals must be collected first. This process varies from one country to another and from one continent to another. Therefore, countries from the European Union collect about 800.000 tones of polyester offals per year. In the United States of America, 1.8 millions of tones/year. In Romania, about 1000 tones/year, and the total amount is of 381.000 tones of offals /year.

Recycling these offals means their re-introduction to the economic circuit. By the recycling of one tone of plastic, we save 1.8 tones of oil and earn 6m^3 of storage space at the garbage hole. One recycled plastic bottle saves the energy necessary for the functioning of one electric bulb for 6 hours. Plastic is one of the materials which may have various “lives”, being able to be recycled several times. We appreciate that PET offals mean 3% of the entire quantity of packaging and according to the details of the plastic manufacturer association in Europe, 1.296.000 PET bottles are collected every hour on the continent.

The recycling methods of PET offals may be grouped in two categories:

1. Offals melting and the polyethylene terephthalate recovery as powder, granules, for the processing with or without adds as to obtain packaging, toys, thin sheets, pipes (US Patent 3696085, 1972; US Patent 3935169, 1976; US Patent 4388356, 1983; US Patent 4543364, 1985; US Patent 4405556, 1983; US Patent 4511322, 1985; US patent 4722820, 1985; US Patent 5503790, 1994).

2. The recovery of the terephthalic acid and the impure or pure ethylene glycol using the polyethylene terephthalate hydrolysis in liquid environment, at the pressure of 100 atmospheres and the temperature of 350°-400°C (US Patent 4358175, 1980; US Patent 5095145, 1992).

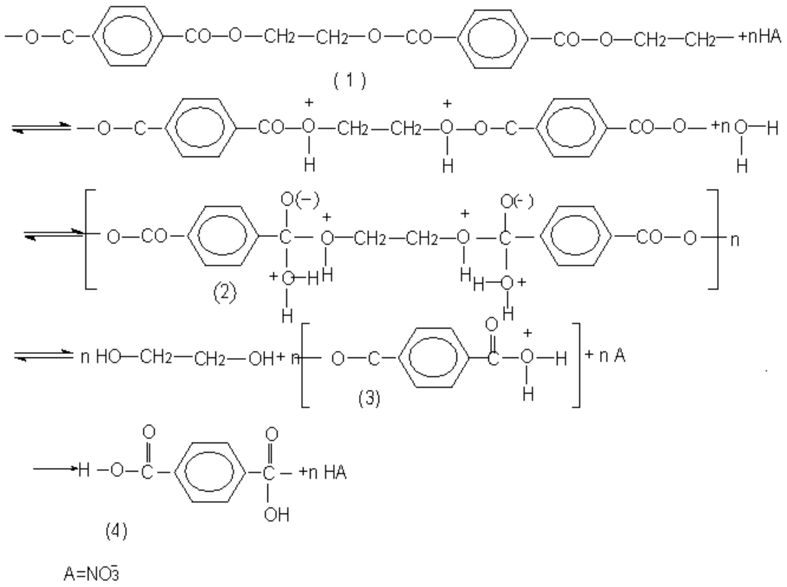
This paper presents an original procedure to obtain the terephthalic acid out of polyester offals for their reintroduction into a new cycle of production (Patent RO 121596, 2007).

Experimental part

Materials and method

Principle of the method

For PET depolymerisation (Scheme 1) we used an oxidizing mixture formed of: nitrogen acid, chloride acid, cuprum chloride and ammonium metavanadate to a gavimetric ratio of 1:7 as compared to the polymers. The reaction means the oxidizing attack on the polymer chemical connections, in 2 phases, obtaining the pure terephthalic acid with great output. The oxidizing attack takes place both on the ethylene connections and on the ester ones. By the catalytic oxidation reaction, the ester groups break in a snapshot, after which, by successive oxidizing processes, they turn into acid groups, according to the reaction mechanism below (Becker and Berger, 1982; Patent RO 121596, 2007; Hendrickson and Cram, 1976; Mager, 1979).



Scheme 1

In the first phase, in a strong oxidizing environment, the addition of a proton to the oxygen atom in the ester group takes place, forming an oxoanion. The reaction takes place very quickly, in the entire polyester melting mass. In the second phase, it takes place an SN_2 nucleophyle replacement, that is the attack of a water molecule upon the carbon atom at the carbonylic group from the structure of compound no.1, forming an unstable intermediary (2). As the water molecule gets close to the carbon from the carboxylic group, the alcoholic group gets away from the ester, forming an unstable intermediary compound (3), which, under the influence of the A^- ($-NO_3^-$) cation rebuilds the oxidizing agent and forms the terephthalic acid (4). At the same time, the ethylene glycol come out at the polymer decay suffers splitting and oxidation reactions, catalyzed by the same oxidizing mixture, forming as intermediary aldehydes or cetones, that are finally oxidized by carbon and water.

Apparatus

The analyses were performed using a Spectrometer FT IR VARIAN 640.

Materials

The following categories of materials were used in the experiments: PET-brokes; nitrogen acid 63-65%; chloride acid 37%; cuprum chloride; ammonium metavanadate.

Oxidizing mixture preparation

The oxidizing mixture is formed of 570 grams of nitrogen acid, 30 grams of chloride acid, cuprum chloride 0.05% and ammonium metavanadate 0.01%.

Completion of the depolymerisation reaction

In a metallic vessel, we weighed 50 grams of broken PET, which were melted at the temperature of 230-250°C until getting a fluid solution. The melted solution was stirred in the oxidizing mixture, which was first heated at 80-90°C. A solid, spongy and brittle mass is formed immediately, accompanied by a massive release of sodium oxides. The solid mass was separated by the oxidizing mixture, introduced into a mortar and broken into pieces until getting a fine paste. Equal parts of this were introduced into 5 glass balloons, provided with ascendant refrigerating agents. The proof from the first balloon was screened, washed several times with water until the oxidizing mixture is completely removed, and then dried. Over the fine paste from balloons no. 2, 3, 4, 5, 70 grams of oxidizing mixture were introduced. Proves 2, 3, 4, 5 were introduced into an electrical apparatus and heated until the ebbing. After the proof gets to the temperature of

90°C the reaction becomes strongly exothermal, the temperature from the reaction balloon getting to 110-120°C. Every 10 minutes the proves are removed from the heating source and cooled in cold water at room temperature. The proves were screened, and the obtained crystals were washed several times with distilled water until the complete removal of the oxidizing mixture, and then introduced into a drying stove and dried for 3 hours at 120°C.

Proves were analysed with FT IR spectrometry, as compared to the terephtalic acid standard, and the analysis results are presented in Figs. 1-7.

Results and discussions

In Fig. 1 the FT IR spectrum of the pure terephthalic acid is presented. The FT IR features, specific to the terephthalic acid are: in the field of the wavelength: λ=700-900 cm^{-1} the strips specific to the benzene nucleus appear. The strips from the wavelength λ=779.629 cm^{-}1, λ=878.505 cm^{-1} and λ=931.035 cm^{-1} are ascribed to the deformation vibration =C-H from the benzene nucleus 1.4 disubstituted. The strip from the wavelength λ=1572.097 cm^{-1} is ascribed to the vibration -C=C from the aromatic nucleus of the terephthalic acid.

The band from the wavelength λ=1673.096 cm^{-1} is ascribed to the carbonyl vibration –C=O from the carboxylic group. The strips from the wave field λ=3000-2500 cm^{-1} are ascribed to the vibration –O–H coming from the carboxylic groups of the terephthalic acid.

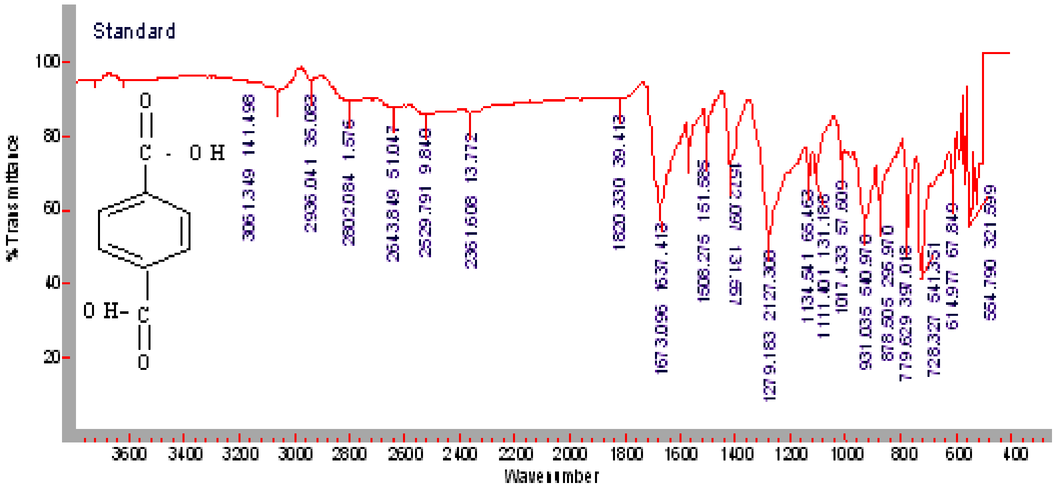


Fig. 1. IR Terephthalic acid spectrum - standard

In Fig. 2 the FT IR spectrum of proof 1 is presented, containing the product coming out after the attack of the oxidizing mixture on the melting of the PET polymer, at t_0 moment. In this spectrum, the strips at the wavelength λ=700-931cm^{-1} can be found, which are ascribed to the vibrations of the disubstituted aromatic nucleus. As compared to the spectrum in Fig.1, in the spectrum from Fig. 2, there is an additional strip at the wavelength λ=1727,930 cm^{-1} which is ascribed to the carbonyl vibration–C=O from the ester group contained by the PET polymer.

Nearby this group, there is another strip, at the wavelength λ=1690,890 cm^{-1} ascribed to the carbonyl vibration –C=O from the carboxylic group of the terephthalic acid. In the field of the wavelength λ=3000-2500cm^{-1} there are strips ascribed to the –O–H vibration from the carboxylic group, but there is also the wavelength λ=1018.306 cm^{-1} a strip ascribed to the –OH–vibration coming out of the primary alcohol, which means that in the first step of the reaction, the ester connections from the PET polymer were broken and the glycolic monoester of the terephthalic acid was formed.

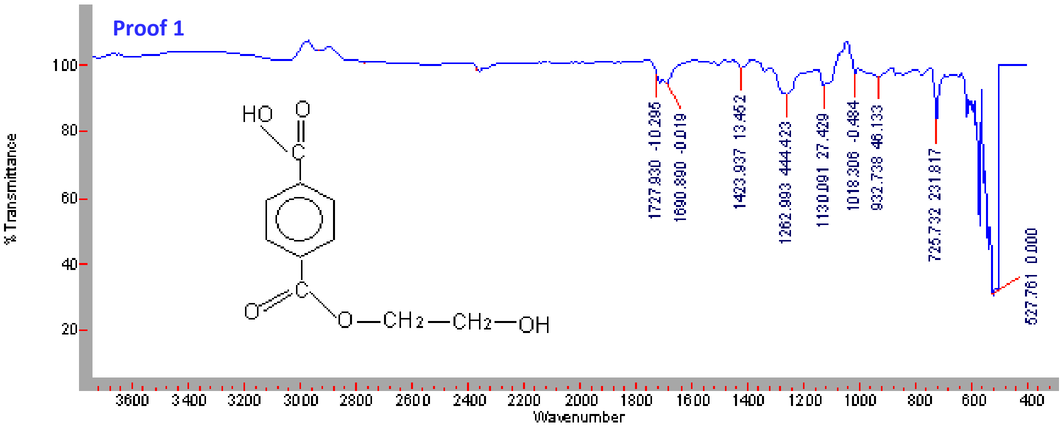


Fig. 2. IR spectrum proof 1

In Fig. 3 the FT IR spectrum of proof 2 is presented, representing proof 1, stirred for 10 minutes with oxidizing mixture. In this spectrum, there are all the strips, as well as in the spectrum from Fig.1, with the exception of the 2 strips nearby from the wave length λ=1690.618cm^{-1} and λ=1712.418cm^{-1} specific to the carbonyl group vibrations–C=O from the carboxylic and ester group.

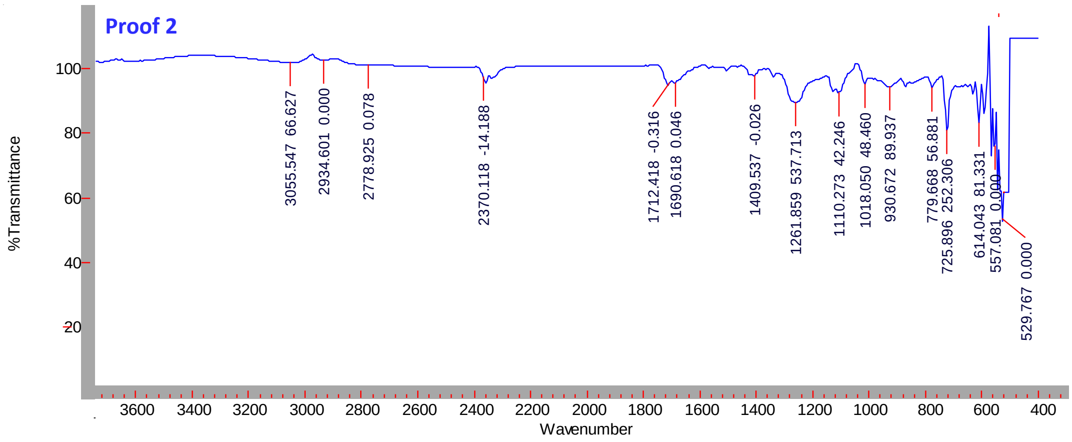


Fig. 3. IR spectrum proof 2

In Fig. 4 the FT IR spectrum of proof 3 is presented, containing proof 1 stirred for 20 minutes with the oxidizing mixture. In this spectrum, we may see that the strip from the wavelength λ=1712.673cm^{-1}, representing the carbon vibration from the ester group got very little, while the strip from the wavelength λ=1678.318cm^{-1} ascribed to the carbonyl vibration –C=O from the carboxylic group is increasing; the other strips are identical as the spectrum in Fig. 1.

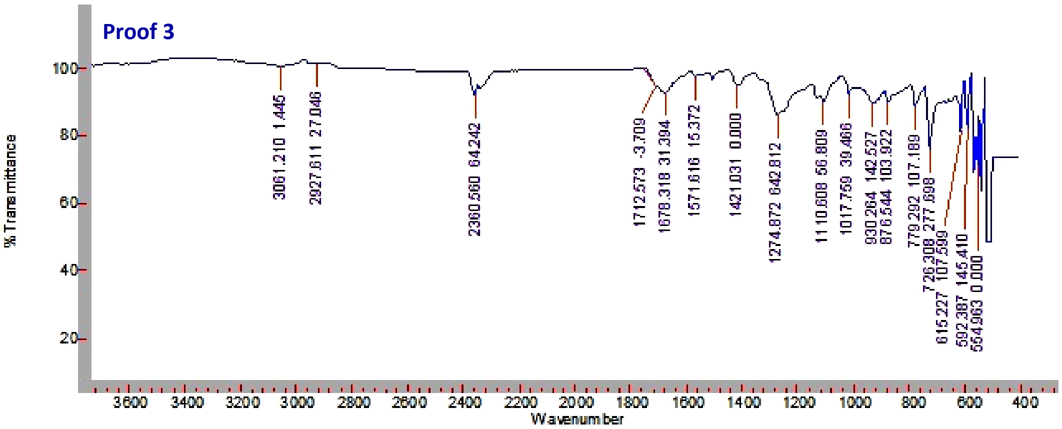


Fig. 4. IR spectrum proof 3

In Fig. 5 the FT IR spectrum of proof 4 is presented, containing proof 1 stirred for 30 minutes, with oxidizing mixture. We may see that the strip from the wavelength λ=1712cm^{-1} ascribed to the carbonylic vibration –C=O of the ester group is completely gone and the only strip which remains is the one from the wavelength λ=1675.860 cm^{-1} attributed to the carbonyl vibration from the carboxylic group –C=O, which means that the transformation reaction of the polymer in terephthalic acid is practically finished. All the strips from Fig.1 can also be seen in Fig.5.

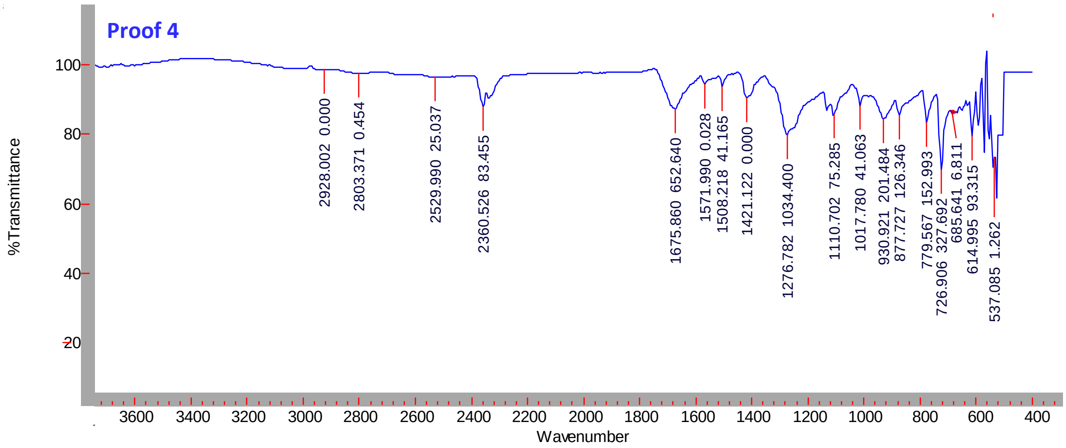


Fig. 5. IR spectrum proof 4

Figure 6 presents the FT IR spectrum of proof 5 containing proof 1, stirred for 40 minutes with the oxidizing mixture. In this spectrum, we may see the similarity between Fig. 1 and Fig. 5, meaning that the reaction is finished and the entire PET polymer turned into terephthalic acid.

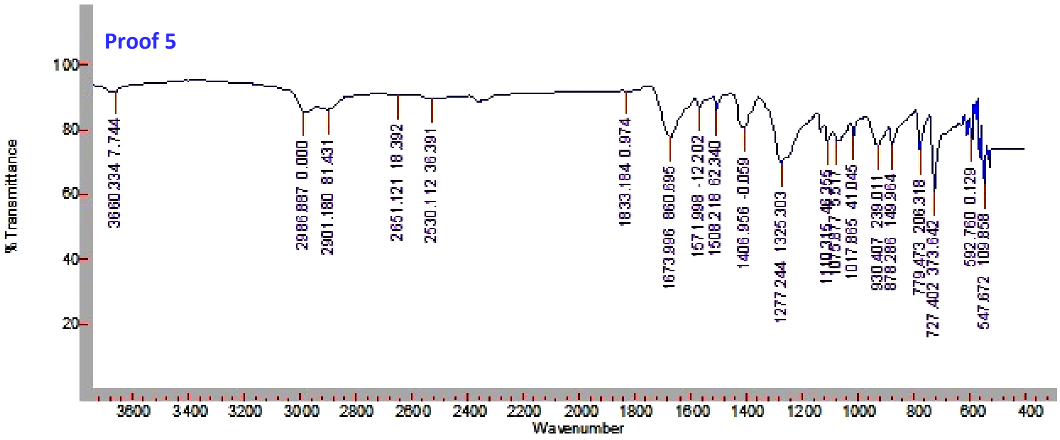


Fig. 6. IR spectrum proof 5

Figure 7 contains the spectrum of the terephthalic acid, presented in Fig.1, and over it the spectrum from Fig.5 and 6 are overlapped. Strips from the spectrum in Fig. 5 and 6 overlap perfectly on the strips from the spectrum in fig., which means that there is only one product, namely the terephthalic acid.

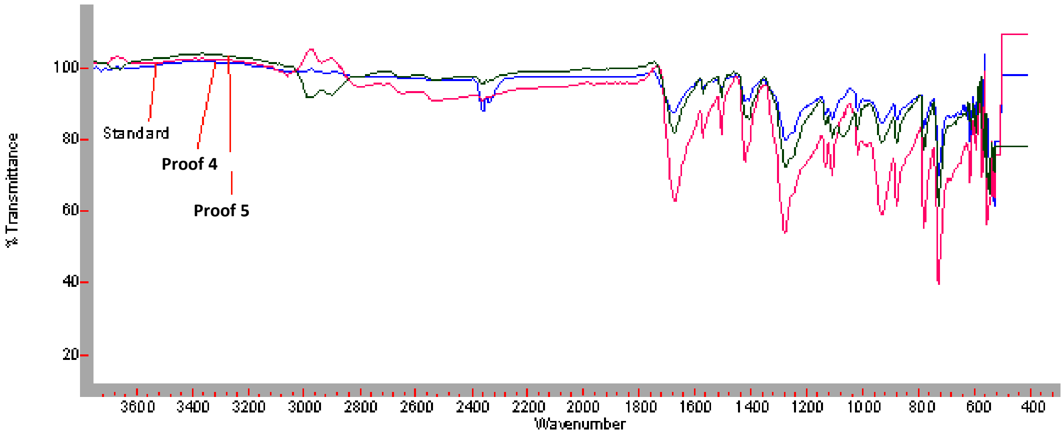


Fig.7. IR spectrum of the terephthalic acid-standard and of proves 4 and 5

4. Conclusions

The terephthalic acid was obtained from PET offals (polyethilenterephthal) using the interaction between the PET melting and the oxidizing mixture made of 95% nitrogen acid 63-65%, 5% chloride acid 37%, 0.01% ammonium metavanadate, 0.05% cuprum chloride as compared to the oxidizing mixture.

The obtaining procedure for the terephthalic acid out of PET offals takes place in two phases. The first one is the interaction between the PET melting and the oxidizing mixture, which is a very strong reaction with nitrogen oxide release, forming a spongy, brittle mass from the breaking of the ester connection, by forming the glycolic monoester of the terephthalic acid. In this phase, the reaction speed is high. In the second phase, the breaking of the 2^{nd} ester connection from the monoester takes place and the oxidation up to the carbon dioxide and water of the ethylene glycol from the splitting reaction, forming the terephthalic acid. The reaction speed in the second phase is low.

The reaction time does not exceed 30 minutes, and the output of the oxidation reaction is between 80-86%.

The procedure to obtain the terephthalic acid out of PET offals may be applied in plants for getting the adipic acid, using the oxidation of the cyclohexanole with oxidizing mixture.

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