UNIVERSIDAD SAN FRANCISCO DE QUITO USFQ

Colegio de Ciencias e Ingenierías

Systematic literature review (LSR): PET depolymerization via alcoholysis

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Ingeniería Química

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RESUMEN

Antecedentes: Se producen anualmente 360 millones de toneladas de plástico en todo el mundo, siendo el Tereftalato de Polietileno (PET) el sexto plástico más producido con el 7,7% de dicha producción. Desafortunadamente, estos tipos de plásticos se eliminan más fácilmente porque se utilizan en productos de un solo uso. El reciclaje tradicional de PET no ha podido solucionar el problema medioambiental. La alcohólisis del PET es un método de reciclaje químico con gran proyección de futuro, sin embargo, su desarrollo a nivel científico e industrial aún es escaso. Hasta la fecha no se ha realizado una revisión bibliográfica sistemática actualizada sobre el tema.

Métodos: Se realizó una revisión literaria sistemática del proceso de despolimerización de PET vía alcohólisis. Para esto se utilizaron cuatro bases de datos electrónicas: Science Direct, Elsevier, Research Gate, and Scopus. Adicionalmente, se utilizó el servicio de librería digital Google Scholars. Estos servicios digitales fueron utilizados entre el 25 de junio y el 3 de julio de 2020.

Resultados: se encontraron 49 resultados, de los cuales 22 fueron artículos de investigación y 27 revisiones. Se observó que los productos más generados fueron dimetil tereftalato (DMT), dioctil tereftalato (DOTP) y dietil tereftalato (DET). Mientras que los alcoholes más utilizados fueron metanol, etanol y alcohol isooctílico. También se determinó que, en la mayoría de los casos, el proceso químico no utilizó un catalizador o, a su vez, intentó encontrar un nuevo catalizador para acelerar el proceso.

Conclusiones: Se demostró que el término "alcohólisis" se ha expandido a nivel mundial durante la última década. Sin embargo, la escasa investigación de nuevos procedimientos de alcohólisis ha limitado este procedimiento. En la mayoría de los casos, no fue posible realizar una comparación profunda de los métodos de despolimerización del PET. Además, se puede encontrar cierta confusión con respecto a la relación aparente entre la glucólisis y la alcohólisis.

Palabras clave: Tereftalato de Polietileno (PET), Alcohólisis, Despolimerización, Reciclaje Químico, Pirólisis.

ABSTRACT

Background: 360 million tons of plastic are produced annually worldwide, being PET the sixth most produced plastic (approx. 7.7% of total plastic production). Unfortunately, these types of plastics are more easily disposed due to its single-use nature. Traditionally, recycling has not been able to solve the environmental problem. The alcoholysis of PET is a chemical recycling method with great future projection, however, its development at a scientific and industrial level is still scarce. To date, an updated systematic literature review on the subject has not been carried out.

Methods: A systematic literary review of the PET depolymerization process via alcoholysis was carried out. For this, four electronic databases were used: Science Direct, Elsevier, Research Gate, and Scopus. Additionally, the Google Scholars digital library service was used. These digital services were used between June 25 and July 3, 2020.

Results: 49 results were found, of which 22 were research articles and 27 were reviews. It was observed that the most generated products were dimethyl terephthalate (DMT), dioctyl terephthalate (DOTP), and diethyl terephthalate (DET). While the most used alcohols were methanol, ethanol, and isooctyl alcohol. It was also determined that in most of the cases, the chemical process didn't use a catalyst or, in turn, tried to find a new catalyst.

Conclusions: It was shown that the term "alcoholysis" has expanded worldwide during the last decade. However, little research into new alcoholysis procedures has limited this procedure. In most cases, a thorough comparison of PET depolymerization methods were not possible. Additionally, some confusion can be found regarding the apparent relationship between glycolysis and alcoholysis.

Keywords: Polyethylene terephthalate (PET), Alcoholysis, Depolymerization, Chemical Recycling, Pyrolysis.

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INTRODUCTION

Polyethylene terephthalate (PET) is a high-strength, low-cost, and easily recyclable synthetic polymer (Pudack et al., 2020). Since 1950, the world production of PET has grown exponentially. In 2018, PET ranked as the sixth most used plastic, reaching 7.7% of world plastic production (ac. 360 million tons) (PlasticsEurope, 2019). PET is generally used in the production of single-use products such as bottles for the packaging of water and soft drinks (Welle, 2011). Reason why its use generates large amounts of plastic garbage, which are usually disposed of in rivers, oceans, and landfills (Du et al., 2019).

PET degradation time (approx. 450 years) makes its impact on marine and terrestrial ecosystems a long-term problem (R. Geyer et al., 2017). Therefore, in the last decade, the recycling of plastic was promoted all around the word as an economically and environmentally profitable processes that allow the generation of various products of commercial interest. Unfortunately, the results show a worldwide disparity in the percentage of recycled PET. Europe, for its part, recycled more than 50% of PET in 2010. While the United States, another large producer and consumer of plastic, only recycled 28% of PET in the same year (B. Geyer et al., 2016). There are no official data from underdeveloped countries, however, it is estimated that on average these countries do not recycle more than 50% of PET (Tsakona, M. & Rucevska, I., 2020). This data shows how this global problem is still far from being solved. Furthermore, the exponential increase in the use of PET plastic, surely, has aggravated this situation.

PET recycling methods can be classified into two groups: “i. Mechanical recycling and ii. Chemical recycling” (Grigore, 2017) (see Figure 1 for a schematic comparison of each technology). Mechanical recycling is based on purely physical processes that are used to produce clean PET flakes (Glaser, 2017). This recycling method is the most popular due to its simplicity and low investment cost. However, this method has some important limitations during its use. PET flakes cannot be infinitely reused, limiting this recycle process in two or three times.

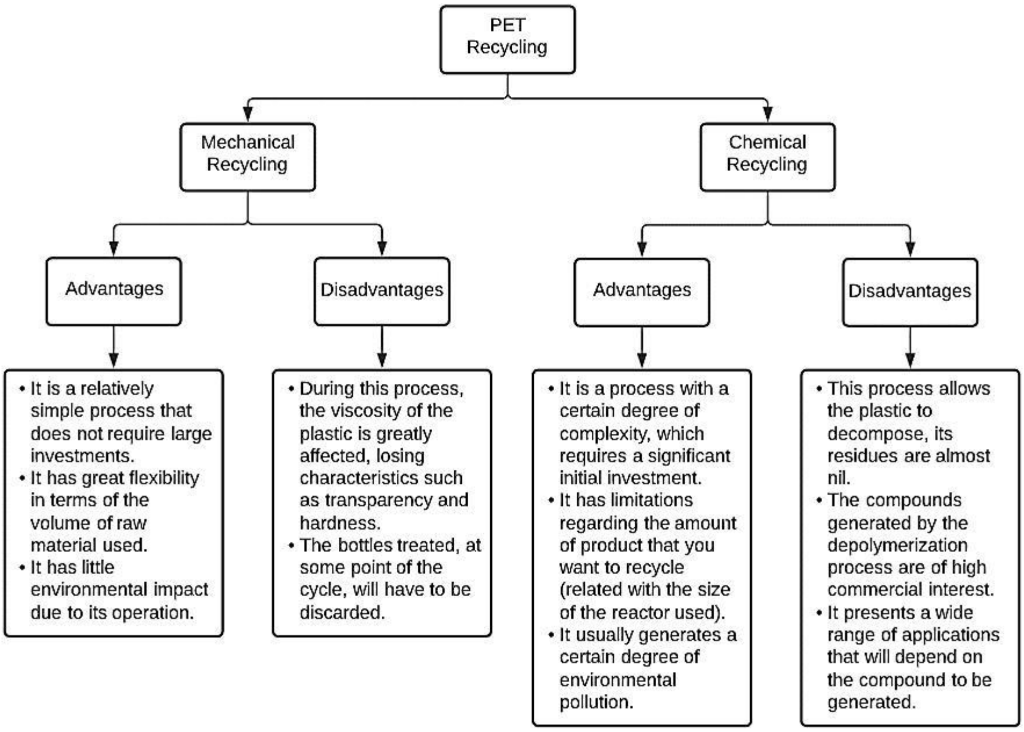


Figure 1. Mechanical and Chemical Recycling Comparison.

On the other hand, chemical recycling seems to be an assertive and applicable solution for present and future generations. It is a reaction-based process, in which PET is depolymerized, breaking down its molecules, using a specific organic compound, to crop new products with high industrial interest. Chemical recycling can be classified by the source used as: i. solvolysis and ii. pyrolysis. Solvolysis is a process of degradation of PET using solvents, while pyrolysis is a process of degradation using heat (Al-Sabagh et al., 2016). Based on the solvolysis process, chemical recycling can be classified into 4 categories: (1) glycolysis, (2) alcoholysis, (3) aminolysis, and (4) hydrolysis (Nishida, 2011). (See a brief explanation in Figure 2).

[redacted]

Figure 2. Most Common Chemical Recycling Methods.

Despite presenting great environmental and economic benefits, chemical recycling has not yet been fully implemented at the industrial level. Currently, glycolysis has only been studied and implemented at an industrial level, without generating a major impact within the PET recycling industry. Hydrolysis and aminolysis, for their part, have been ruled out due to their high production cost and the high complexity of their processes (Niaounakis, 2019). PET alcoholysis, on the other hand, is a relatively new process based on the use of alcohol, in which different products of high commercial interest can be generated. Alcoholysis of PET has gained relevance in recent years. This technique could present a real solution to the problem of recycling PET bottles. Even though many studies related to this type of chemical recycling have been carried out, the information is not disclosed or collected. Few scientific articles present all the possible products that can be produced within the chemical recycling process by alcoholysis depending on the alcohol used, the type of catalyst, or even operational factors such as temperature and reaction time. For this reason, this Systematic Review of Literature seeks to study in-depth the existing scientific trends in the study of PET alcoholysis in the last ten years, generating a document that can serve as a guide for future scientific research.

RESEARCH METHODOLOGY

The main objective of the systematic literature review is to identify and summarize the most important parameters and results obtained from the research carried out about PET alcoholysis, encouraging future research related to the implementation and development of alcoholysis in the scientific and industrial field. The model proposed for this systematic literature review is based on the Fink model, which consists of the use of five general guidelines (see Figure 3 for a brief explanation).

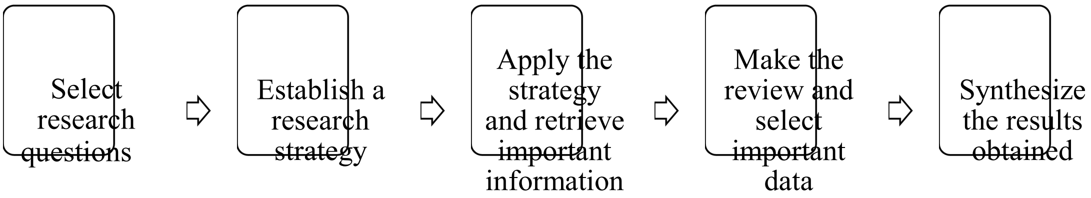


Figure 3. Fink literature review method used in this work.

Source: Fink, 2014.

Research questions

The first step of the systematic literature review consists in the determination of the research question(s) that will be used as a guide within the literary analysis process. For this systematic literature review, three questions were selected:

- Is there a significant advance in the scientific study of alcoholysis in the last 10 years?
- Can similar results be obtained with different chemical reagents and catalysts?
- What role do operation conditions, such as temperature, pressure, and reaction time, play in the alcoholysis of PET?

Research strategy

Once the research questions were determined, the next step was the creation of a systematic research strategy. For this, two sections were developed: selection of the literary sources that were used in the review and the determination of the search terms that were implemented during the research. For the first section, four electronic databases were selected: Science Direct (sciencedirect.com), Elsevier (elsevier.com), Research Gate (researchgate.net), and Scopus (scopus.com). Additionally, the Google digital library service was used: Google Scholars (scholar.google.com). Subsequently, for the second section, the search terms were determined based on a pre-review made by the author. This process consisted on the investigating the topic of chemical recycling as an introductory way to understand the process and its implications. Later, a deeper investigation was realized, focusing on PET alcoholysis. This process helped to determine that the words “PET ALCOHOLYSIS” were not enough to delimitate the topic of interest. Most of the results obtained in the electronic databases were not directly related to PET alcoholysis as their central field of study, but rather that, these terms were cited in the text as an introductory topic of other chemical recycling processes. Having analyzed the PET alcoholysis process, DEPOLYMERIZATION was determined as a search keyword. Therefore, "PET AND Alcoholysis AND Depolymerization" was determined as the search terms, getting better results in contrast with the ones obtained at the beginning. Finally, a publication date delimitation was made between 2010-2020, accepting only English-speaking articles.

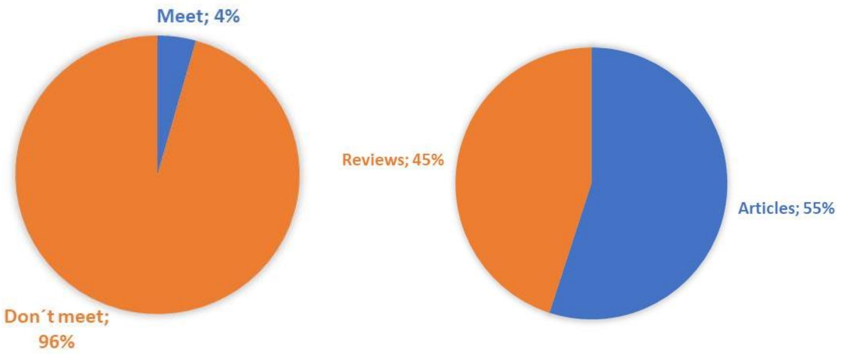
Selection and synthesis of the obtained results

The search process was carried out in 2020 between June 25th and July 3rd. During the development of this literary review, a total of 1192 results were obtained. Results were distributed as follows: Google Scholars (793 results), Direct Science (15 results), Elsevier (210 results), Research Gate (121 results), Scopus (53 results). The screening of the results was made at par with the digital research. This method allowed the realization of individualized analysis of each result obtained while the review was made in the selected digital sources. Only scientific publications were selected, leaving aside any other type of additional resources such as textbooks, patents, etc. Finally, a scientific journal was created to organize all the information that can be useful for the accomplishment of the research questions established above. For reader's ease, the selected publications were classified by the alcohol used, the product obtained, the catalyst used and the author reference (see Table 1 for more information about these results).

DESCRIPTIVE ANALYSIS

Distribution of results by type and publication year

The process of classification was made individually. In that process, all the results were analyzed to determine if they met the research conditions established in this document. From the 1192 results obtained in the research, just 49 scientific publications were of direct interest for this systematic literature review, meaning that just 4% of the results were directly related with PET depolymerization via alcoholysis (see Figure 4a). On the other hand, it was found that of these 49 results, 22 publications (45%) were research works related to the alcoholysis process, while 28 publications (55%) were reviews related to chemical recycling in general. It seems like the subject of alcoholysis solely, maintains a relatively low research interest, where 6 out of 10 publications made in the last 10 years were reviews and just 4 of them were studies about the process. As much as the author knows, non-reviews related directly to PET alcoholysis methods could be found, demonstrating the importance of this work.



(a) (b)

Figure 4. Distribution of results (a) by their application to the LSR and (b) type of publication.

One of the objectives of this document was to determine if there has been an increase in scientific interest for the subject of PET alcoholysis. For this, a publication year analysis was made. It was found that the distribution of articles published in the last 10 years does not follow any path. However, it can be seen in Figure 5 that 2019 was the year with more results found, and 2020 is shaping up to be an equally productive year. This considering that the literature review was carried out in the middle of the year, leaving aside articles published in the last section of the year. Figure 5 also makes a distinction between the type of the publications obtained. Twenty-two research articles were obtained from the last 10 years. It was found that in the last two years a total of 7 publications were published, thus, being the highest number of scientific contributions (32%) during the last decade, demonstrating the notoriety that alcoholysis has obtained at scientific level.

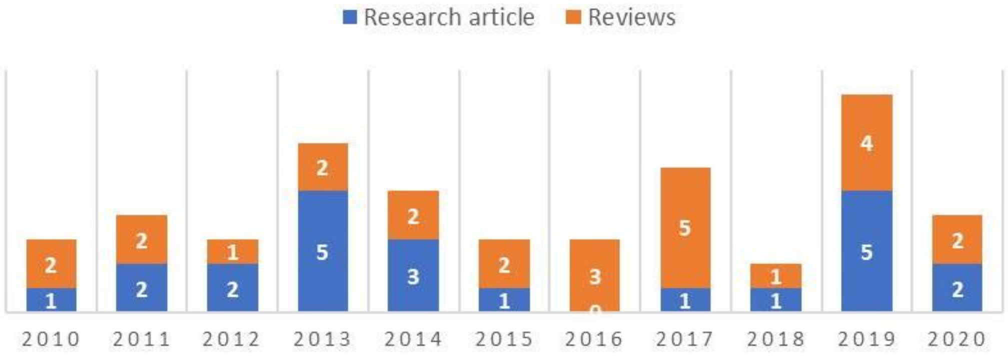


Figure 5. Distribution of obtained articles by publication year and type.

The use of catalyst and alcohols in alcoholysis processes

The selection of a specific alcohol is imperative during the PET alcoholysis, although the depolymerization process via alcoholysis follows a similar route for all alcohols that present an -OH group. Before stablishing any process, it is necessary to establish the type of product that is going to be produced. The alcoholysis process is not an economical recycling method, therefore, the type of product obtained must satisfied specific market needs. For this reason, it is important to evaluate all the different combinations that can be made during the PET alcoholysis process. In addition, the selection of a catalyst is equally important. It can modify the kinetics of the reaction, altering factors such as temperature and reaction time, and making the process much more efficient and even more profitable. For that reason, in Table 1 shows a summary of the different combinations that can be carried out during the PET depolymerization via alcoholysis. This table organize the information in alphabetic order depending to the product that can be produced.

Table 1. Results of the literature research.

Article Name	Alcohol Used	Catalyst	Products	Reference
Chemical Recycling of PET Waste with Multifunctional Pentaerythrytol in the Melt State	Pentaerythritol	Zinc Acetate	Bis(tri-hydroxylneopentyl) terephthalate (BTHNPT)	(Mendes et al., 2011)
Butanol Alcoholysis Reaction of Polyethylene Terephthalate Using Acidic Ionic Liquid as Catalyst	Butanol	Zinc chloride	DBTP	(S. Liu, Wang, et al., 2013)
PET and aluminum recycling from multilayer food packaging using supercritical ethanol	Ethanol	Not used	DET	(Fávaro et al., 2013)

PET depolimerization in supercritical ethanol conditions catalyzed by nanoparticles of metal oxides	Ethanol	Cobalt and Nickel oxides	DET	(Rodrigues Fernandes et al., 2020)
PET depolymerisation in supercritical ethanol catalysed by [Bmim][BF4]	Ethanol	[Bmim][BF$_4$]	DET	(Nunes et al., 2014)
Poisoning Effects of Water and Dyes on the [Bmim][BF4] Catalysis of Poly (Ethylene Terephthalate) (PET) Depolymerization under Supercritical Ethanol	Ethanol	[Bmim][BF$_4$]	DET	(Nunes et al., 2017)
Heterogeneous continuous kinetics modeling of PET depolymerization in supercritical methanol	Methanol	Not used	DMT	(Genta et al., 2010)
Investigating and modeling PET methanolysis under supercritical conditions by response surface methodology approach	Methanol	Not used	DMT	(Q. Liu et al., 2015)
Recycling of poly (ethylene terephthalate) waste through methanolic pyrolysis in a microwave reactor	Methanol	Zinc Acetate	DMT	(Siddiqui et al., 2012)

Synthesis of gasoline and jet fuel range cycloalkanes and aromatics with poly (ethylene terephthalate) wastes	Methanol	Not used	DMT	(Tang et al., 2019)
ZnO nanodispersion as pseudo homogeneous catalyst for alcoholysis of polyethylene terephthalate	Methanol	Zinc Oxide	DMT	(Du et al., 2020a)
Mechanism of Depolymerization Reaction of Polyethylene Terephthalate: Experimental and Theoretical Studies	Ethanol, 1-propanol, 1-hexanol	Not used	Disodium terephthalate	(Asakuma et al., 2011)
Alcoholysis of PET to produce dioctyl terephthalate by isooctyl alcohol with ionic liquid as cosolvent.	Isooctyl alcohol	Zinc Acetate	DOTP	(Chen et al., 2014a)
Alcoholysis of poly (ethylene terephthalate) to produce dioctyl terephthalate with sub-and super-critical isooctyl alcohol	Isooctyl alcohol	Not used	DOTP	(F. Liu et al., 2013)
Alcoholysis of Polyethylene Terephthalate for Dioctyl Terephthalate Using Choline Chloride-Based Deep Eutectic Solvents as Efficient Catalysts	2-ethyl-1-hexanol	$ChCl/Zn(Ac)_2$	DOTP	(L. Zhou et al., 2019)

Isooctanol alcoholysis of waste polyethylene terephthalate in acidic ionic liquid	Isooctyl alcohol	($[HO_3S-(CH_2)_3-NEt_3]Cl-FeCl_3$)	DOTP	(S. Liu, Zhou, et al., 2013)
Kinetics of alcoholysis of poly (ethylene terephthalate) in sub- and super-critical isooctyl alcohol to produce dioctyl terephthalate	Isooctyl alcohol	Not used	DOTP	(Ding et al., 2014)
Oligoester and Polyester Production via Acido-alcoholysis of PET Waste	Ethylene glycol	Not used	Oligomers	(Kárpáti et al., 2018)
Structure and thermal properties of various alcoholysis products from waste poly (ethylene terephthalate)	Dihydric alcohols	n-Butyl titanate	Oligomers	(X. Zhou et al., 2019)
Recycling of Off-Grade PET via Partial Alcoholysis to Synthesize Functionalized PET Oligomer Nanocomposites	Ethylene glycol	Manganese Acetate	Oligomers	(Barkoula et al., 2012)
PET Recycling by Alcoholysis Using a New Heterogeneous Catalyst: Study and its Use in Polyurethane Adhesives Preparation	Diethylene glycol	Sodium metasilicate	PET-polyol	(Scremin et al., 2019)
Eco-friendly synthesis of PET-based polymeric plasticizer and its application in nitrile-PVC rubber blends	Butanol	Zinc chloride	Polymeric plasticizer	(Sirohi et al., 2019)

Synthesis and characterization of polymeric plasticizer from PET waste and its applications in nitrile rubber and nitrile–PVC blend	2-ethyl-1-hexanol	Not used	Polymeric plasticizer	(Dutt & Soni, 2013)

The data obtained by screening were processed, looking for certain trend lines regarding the use of the reagents used by the authors in Table 1. Figure 6 shows the frequency of use of certain types of alcohol to carry out the alcoholysis process. This graph shows a certain trend regarding the use of certain alcohols such as ethanol, methanol, and isooctyl alcohol. Furthermore, it is found that 3 of the cited authors (Barkoula et al., 2012; Kárpáti et al., 2019; Scremin et al., 2019) used glycols in the PET alcoholysis process, even though, this compound is generally used in the glycolysis process. On the other hand, in Figure 7, it is observed that there is no clear trend regarding the use of a specific catalyst. This behavior shows that a big part of the authors prefers to work with non-catalytic processes, while some a few others tried to implement new catalysts. In Figure 6 it can be shown that most of the alcoholysis investigation is based on the use of three alcohols (representing more than 63% of the articles) in order to get specific kinds of products.

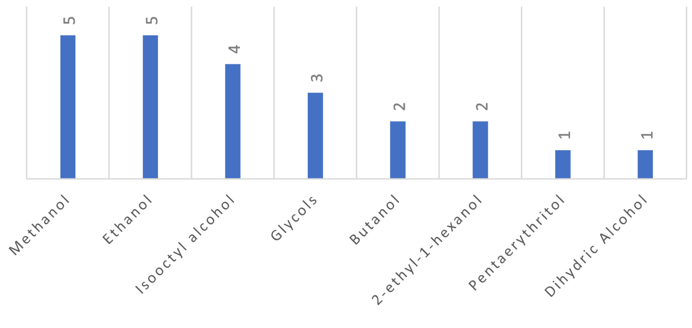


Figure 6. Distribution of alcohols used by the authors of Table 1.

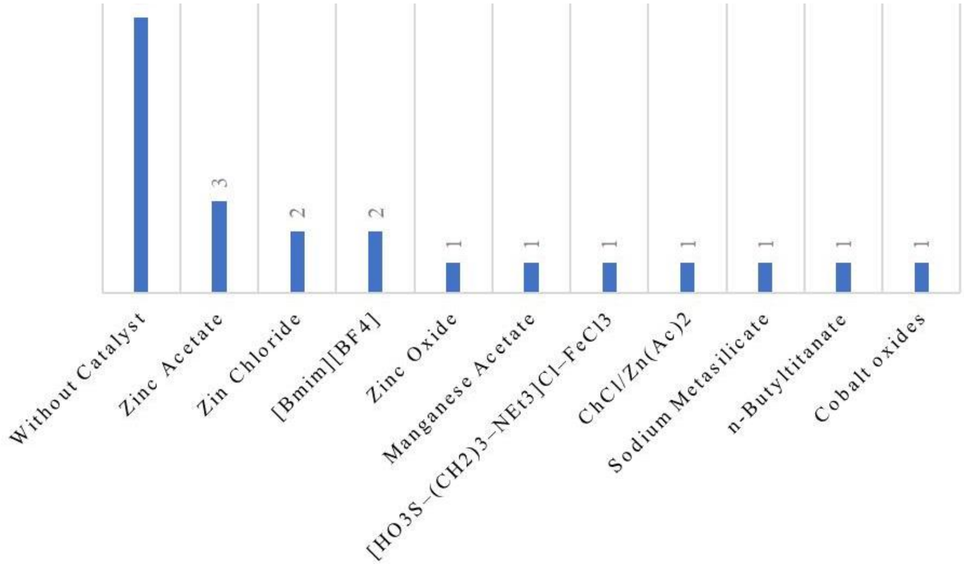


Figure 7. Distribution of catalysts used by the authors of Table 1.

Data analysis of the results according to obtained products

As already mentioned, alcoholysis can generate various products using different alcohols and catalysts. That is why it is important to study the different combinations that can be made to not only maximize production and reduce operating costs, but also promote scientific participation for the investigation of new processes. Figure 8 shows the distribution of the different products obtained by the authors studied in this literary review, which are described below:

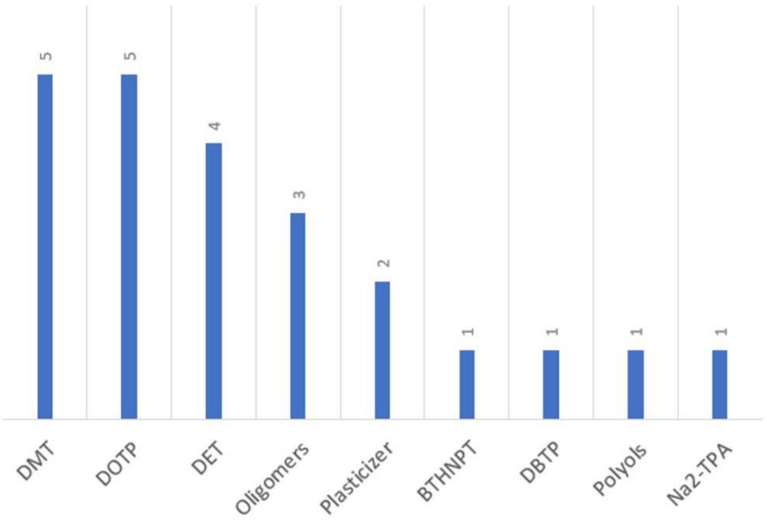


Figure 8. Distribution of products obtained by the authors of Table 1.

Dimethyl terephthalate (DMT) is a chemical compound used within the chemical recycling industry as a base material for the synthesis of PET. The production of DMT occurs through the alcoholysis of PET (see Figure 9 for a better description of the reaction mechanism). This depolymerization process must be carried out using methanol, and it also allows the use of certain catalysts to maximize PET conversion, improve DMT yield, and decrease reaction time and operating temperature. The depolymerization process can be carried out by pyrolysis and by supercritical fluids. The first result found in this literary analysis was published by Siddiqui et al. in 2012, in which a 92.4% PET conversion was reported. For this, the pyrolysis of the PET waste was carried out using 1 gram of zinc acetate for each gram of PET, at 200 °C for 55 minutes, using microwave irradiation (this reaction is described in Figure 9). It was found that this method decreases reaction time, showing that most of the degradation occurred in the first 5-10 minutes.

Liu et al. reported that by applying supercritical fluids it is possible to obtain a DMT yield of 99.79% at high pressure, for which no catalysts were needed but the temperature had to be increased to 298 °C for 112 minutes. Tang et al. showed that the reaction time can favor the depolymerization of PET, obtaining a DMT yield of 97.3%, and carrying out the reaction at the same temperature as Siddiqui et al. (200 °C) but lengthening the reaction time to 3.5 hours and without the presence of catalysts. Later, Du et al. found that the use of ZnO, as a nanodispersion catalyst, allowed to considerably reduce the reaction time to 15 minutes, and a temperature of 170 °C; getting a PET conversion of 97% and 95% yield of DMT. It was also determined that the minimum temperature that can be used to have a high conversion is 160 °C. They use a 4 nm size catalyst that can achieve a 553 g PET/h per gram of ZnO. It was also determined that this catalyst is stable in dispersion after six months.

On the other hand, Genta et al. established a kinetic model for PET depolymerization using supercritical methanol, analyzing the behavior that PET has during the depolymerization process and its consecutive reactions. For this, the authors established mass transfer of MHET as the disturbing factor of the reaction, leaving aside the mass transfer that the other compounds produced within the depolymerization of PET has during the kinetic model. It was found that during the PET depolymerization reaction using supercritical methanol, the reaction followed a first-order rate. Furthermore, MHET was determined to be the most stable product during the reaction. Please refer to Table 2 for a complete summary of works and operation conditions.

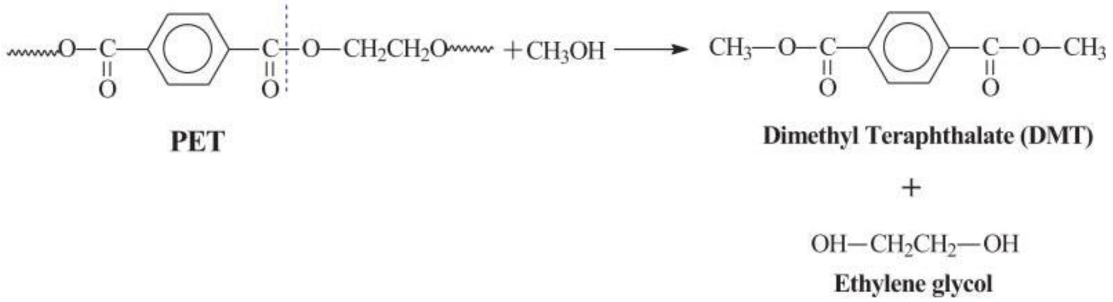


Figure 9. PET depolymerization with methanol to produce DMT and EG.

Source: Siddiqui et al., 2012.

Table 2. Summarized information of the literature review obtained for DMT production.

Reference	**Raw material**	**Particle size of raw material**	**Type of reactor**	**T (ºC)**	**P**	**Other**
(Siddiqui et al., 2012)	PET waste	-----	Microwave reactor (165-200 W)	200	1.2 MPa	Nitrogen atmosphere
(Q. Liu et al., 2015)	PET granules	3 mm diameter	Batch reactor	298	Not constant	stirring (2 Hz)
(Tang et al., 2019)	PET waste	2 mm × 3 mm	Batch reactor	200	-----	Nitrogen atmosphere
(Du et al., 2020)	PET powders	125 µm diameter	Stainless steel autoclave	170	-----	Magnetic stirring (500 rpm)

Dioctyl terephthalate (DOTP) is a polyvinyl chloride plasticizer that is characterized by having no phthalates. Its main use is in the manufacture of PVC. This type of material is the main product of PET alcoholysis when using isooctyl alcohol or 2-ethyl-1-hexanol as the main reagent (see Figure 10 and Figure 11 for a better description of the reaction mechanism). S. Liu et al. proposed the depolymerization of PET waste fibers by using an isooctyl alcohol in conjunction with an ionic acid liquid ([HO_3S– $(CH_2)_3$ – NEt_3] Cl – $FeCl_3$) as a catalyst. This reaction was carried out in a 150 ml flask at 210 °C for 8 hours under reflux. It was obtained 100% PET conversion and a DOTP yield of 97.6%. The ionic liquid was able to be reused up to seven times without affecting its DOTP performance, reaching 93.7%, and PET conversion of 100%. Liu et al. established another method by using the same alcohol, without using any catalysts. The reaction was carried under supercritical and subcritical conditions. In this study, the alcoholysis of PET was made in different temperature condition, from 240 to 340 °C. The production of DOTP has exponentially increased under supercritical conditions (300 °C), but after this temperature, the production of DOTP started to be lost. For this reason, the best operative conditions were at 300 °C for 3 hours obtaining a PET conversion of 100%, and a DOTP yield of 97%. Chen et al. used zinc acetate as a catalyst and ionic liquid [Bmim]Cl as a cosolvent. The reaction generated a PET conversion of 100% and a DOTP yield of 93%, this at 200 °C and with a reaction time of 5 hours. The use of ionic liquids improved the reaction rate, making it easier for the dispersion of PET.

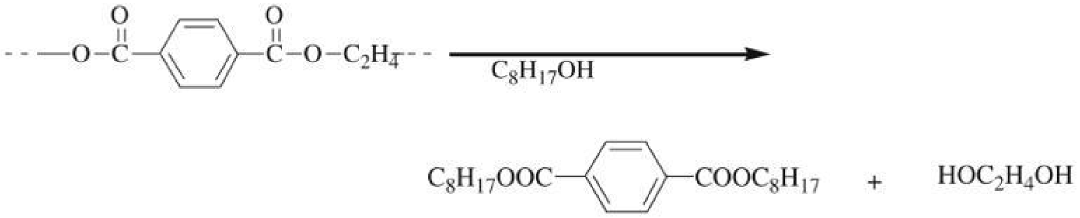


Figure 10. PET depolymerization with isooctyl alcohol to produce DOTP and EG.

Source: S. Liu et al., 2013.

Furthermore, Ding et al. studied the kinetics of PET depolymerization by sub- and supercritical isooctyl alcohol to produce DOTP. This study was made in a batch reactor with a temperature range of 260-380 °C. It was determined that under subcritical conditions the decomposition rate of DOTP was slow, provoking a higher activation energy rate of 82.14 KJ/mol; comparing to 30.20 KJ/mol obtained in supercritical conditions. A pseudo-first order reaction model of PET was also determined, demonstrating that this process is advantageous, but are also sensible respecting to the temperature and the reaction time. Finally, L. Zhou et al. used 2-ethyl-1-hexanol in conjunction with choline chloride-based deep eutectic solvent ChCl/Zn(Ac)$_2$ (also known as DES) as the catalyst. The utilization of this new catalyst was satisfactory. The reaction was carried out at 180 °C for 1 hour, obtaining a PET conversion of 100% and a DOTP yield of 84.7%. It was also determined that the best molar ratio of ChCl and Zn(Ac)$_2$ was 1:1. For this reaction, the activity energy rate was 95.05 kJ/mol. During this investigation, PET conversion and DOTP yield were not studied. Please refer to Table 3 for a complete summary of works and operation conditions.

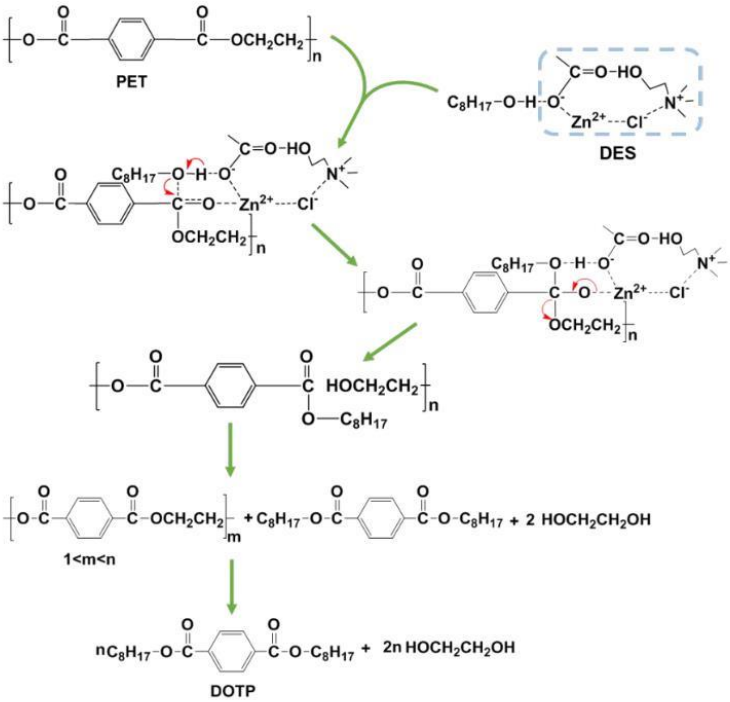


Figure 11. PET depolymerization with 2-ethyl-1-hexanol & DES to produce DOTP and EG.

Source: L. Zhou et al.(S. Liu, Zhou, et al., 2013), 2019.

Table 3. Summarized information of the literature review obtained for DOTP production.

Reference	**Raw material**	**Particle size of raw material**	**Type of reactor**	**T (^{0}C)**	**P**	**Other**
(S. Liu, Zhou, et al., 2013)	PET waste	-----	Flask with a mechanical stirrer	210	-----	Reflux made in a condenser
(F. Liu et al., 2013)	Virgin PET	-----	Batch type auto-clave reactor	300	-----	-----
(Chen et al., 2014b)	Virgin PET	Diameter of 2 mm	Round-bottom three-necked flask	180	0.1 MPa	-----
(L. Zhou et al., 2019)	Virgin PET	Pellets 2x2.5x2.7 mm	Round flask	180	0.1 MPa	Required strong agitation

Diethyl terephthalate (DET) is a diester of organic origin that is mainly used for the direct esterification of terephthalic acid. This process is based on the depolymerization of PET using ethanol (see Figure 12 for a better description of the reaction mechanism) and different catalysts, such as [Bmim][BF_4] and cobalt oxides. The first result obtained in the literary review was carried out by Fávaro et al. in 2013, where the depolymerization process was carried out in supercritical conditions, maintaining a reaction time of 2 hours at 255 °C and a pressure of 11.65 MPa. This reaction was made without the use of a catalyst, getting a DET yield of 80%. For this, the multilayer PET products from the packaging industry were used. This multilayer product was distributed in films that were cut in 200x300 mm pieces. On the other hand, Nunes et al. carried out a related procedure, maintaining a temperature of 255 °C, with a reaction time of 45 minutes and by using [Bmim][BF_4] as a catalyst. This reaction was made on a home-made batch-type reactor made with a capacity of 1 liter. The process permitted the obtention of a DET yield of 98% and a considered reduction of the reaction time compared with other works. Later, Rodrigues et al. carried out the PET depolymerization process by using supercritical ethanol and cobalt and nickel oxide nanoparticles as catalysts. It was observed that cobalt oxide nanoparticles have better results during the alcoholysis, obtaining a yield of 98.17% at 255 °C during a reaction time of 90 minutes. This study also shows that the type and size of the catalyst significantly affected the depolymerization process, showing that nanoparticle catalysts can be extremely good options.

Conversely, Nunes et al. studied the effect that water and dyes have during the alcoholysis of PET in supercritical ethanol. For this purpose, colorless and colored PET flakes of 1 mm were used with different concentrations of ethanol-water and [Bmim][BF_4] as the catalyst. The reaction was made at 255 °C and 115 atm for 45 minutes, getting a DET yield of 98% when the content of water in ethanol was cero. On the other hand, when water content increase to 4% and colored PET were used, the yield of DET decrease to 66% in green PET and 28% in blue PET. Demonstrating that the presence of water and dyes affects the catalytic action during the depolymerization of PET.

Please refer to Table 4 for a complete summary of works and operation conditions.

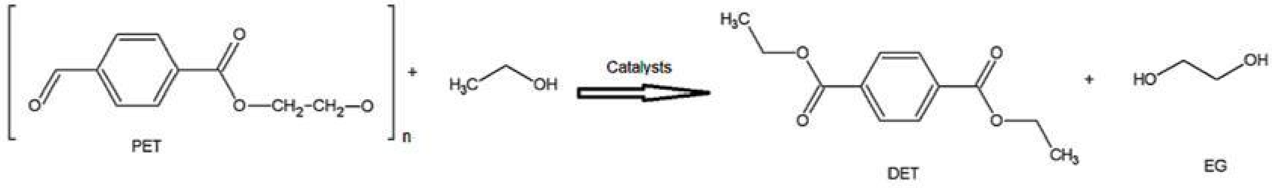


Figure 12. PET depolymerization with ethanol to produce DET and EG.

Source: Rodrigues et al., 2020.

Table 4. Summarized information of the literature review obtained for DET production.

Reference	**Raw material**	**Particle size of raw material**	**Type of reactor**	**T (ºC)**	**P**	**Other**
(Fávaro et al., 2013)	PET waste	Films 200x300 mm	----	255	11.65 MPa	Products precipitate in water
(Nunes et al., 2014)	PET	Pellets ca. 1 mm	Home-made batch reactor of 0.1 liter	255	11.65 MPa	Heating rate of about 8C/min
(Rodrigues Fernandes et al., 2020)	PET waste	3×3×0.5 mm	Home-made batch reactor of 0.1 liter	255	11.65 MPa	Heating rate of about 8C/min
(Nunes et al., 2017)	PET waste	Flakes ca. 1 mm	Home-made batch reactor of 0.1 liter	255	11.65 MPa	Heating rate of about 8C/min

PET Oligomers are molecules which have few identical or similar repeating units within their structure. Its importance lies in the possible application of this type of compound within the preparation of various materials, improving their physical characteristics. This method can be carried out with the use of ethylene glycol and certain catalysts. In this case, the use of partial glycolysis is usually compared and assumed as an alcoholysis process (see Figure 13 and Figure 14 for a better description of the reaction mechanism). Barkoula et al. used ethylene glycol and manganese acetate during partial glycolysis in which he considered as an alcoholysis procedure. The reaction was made at 200 °C for 120 minutes without the use of any catalyst giving a PET oligomer yield of 75.45%. This same result was obtained in 60 minutes at the same temperature, but using manganese acetate as catalyst 0.5% wt. It was also determined that the increase in the degree of polymerization of PET is closely related to the molar ratio of EG and PET, the increase in the amount of catalyst, and the reaction time.

Subsequently, X. Zhou et al. proposed the use of dihydric alcohols and n-Butyltitanate as the catalyst. The reaction was accomplished by different types of dihydric alcohols. It was established that the sample with neopentilglicol got best results with an oligomer yield of 83.6% and a dimer/trimer of 10.5%. For this, the following conditions were used under batch conditions: 210 °C during a reaction time of 5 hours. It could be determined that the use of alcohol with small structures has higher selectivity for the formation of oligomers, dimers, and trimers. Whereas alcohols with large molecular size have a greater tendency to form copolymers without requiring BHET. Finally, it was shown that high temperatures help to improve the reactivity of glycols, thus producing a higher alcoholysis activity.

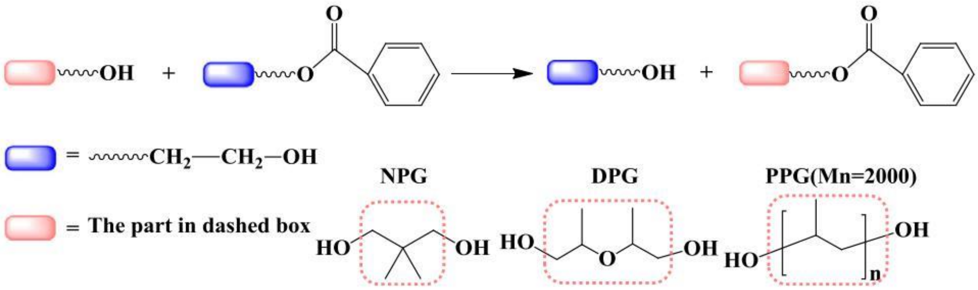


Figure 13. PET depolymerization with dihydric alcohols to produce PET oligomers.

Source: X. Zhou et al., 2019.

Kárpáti et al. produced oligomers by using an acid-alcoholysis method, in which 1,4 butanediol were used in conjunction with different organic acid such as adipic acid, sebacic acid, and succinic acid. The objective of this article was to demonstrate that the acid-alcoholysis process generate products of more uniform structure uniform. PET conversion as well as oligomer yield were not studied. The reaction was carried out at 210 °C for 1.5-2.5 hours. A four-necked round bottom glass flask of 0.25-liters capacity was used. It was found that the reagents used in this process were incorporated within the reaction products, something that helped the obtention of oligoesters with carboxyl and hydroxyl end groups. In all cases, it was found that this process can generate oligoesters which can be used to produce new compostable semi-aromatic polyesters. Please refer to Table 5 for a complete summary of works and operation conditions.

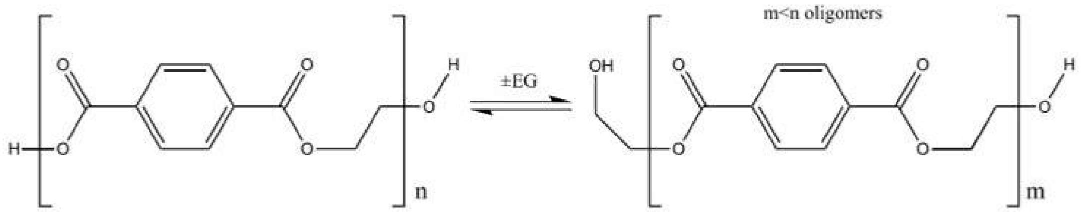


Figure 14. PET depolymerization with EG to produce PET oligomers.

Source: Kárpáti et al., 2018.

Table 5. Summarized information of the literature review obtained for PET oligomers production.

Reference	**Raw material**	**Particle size of raw material**	**Type of reactor**	**T (°C)**	**P**	**Other**
(Barkoula et al., 2012)	Off-grade PET	Amorphous	Home-made reactor with a reflux condenser	200	----	-----
(Kárpáti et al., 2018)	PET waste	Flakes 0.4x10x6.8 mm	Four-necked round bottom glass flask	220	0.1 MPa	Argon atmosphere
(X. Zhou et al., 2019)	PET waste	Flakes 5x5 mm	Four necked glass reactor	210	----	Nitrogen atmosphere

Polymeric plasticizers are substances added to certain materials to make them softer and more flexible so that it can increase its plasticity characteristics. The production process of these plasticizers occurs through the implementation of butanol or 2-ethyl-1-hexanol and some kind of catalyst if preferred. Dutt & Soni studied the PET depolymerization method based on the use of 2-ethyl-1-hexanol. Twelve different conditions were studied on a three-necked round bottom flask of 1 liter of capacity. The best PET conversion to plasticizers was 99.9% for which an operational temperature of 190 °C and a reaction time of 12 hours are required, in conjunction on the applying with a 200-rpm stirrer. The polymeric plasticizer produced presented a density of 0.96, an acid value of 0.42, and a hydroxyl value of 130.50. Finally, it was concluded that the plasticizer produced got better qualities than other common plasticizers such as di-n-octilftalate (DOP).

On the other hand, Sirohi et al. proposed in 2019 the use of Butanol, in conjunction with a $ZnCl_2$ catalyst. The reaction was carried out in a one-necked round bottom flask of 1-liter capacity. The yield of polymeric plasticizer was 93%, and it was obtained by an operating temperature of 190 °C and a reaction time of 4 hours. The plasticizer produced demonstrated better tensile strength, elongation at break, hardness; denoting its best qualities compared to other plasticizers on the market used in the manufacture of PVC.

Bis (tri-hydroxyl neopentyl) terephthalate (BTHNPT) is an organic monomer used as an additive for asphalt and other types of adhesives. The PET depolymerization process to produce this compound is based on the use of pentaerythritol, a multifunctional alcohol (see Figure 15 for a better description of the reaction mechanism). Mendes et al. was the only study who developed a procedure in which zinc acetate was used as a catalyst in conjunction with pentaerythritol. The reaction was carried out at a temperature of 250 °C and stirring at 60 rpm for 10 minutes; 87% of BTHNPT yield was obtained. This study showed that the alcohol used kept the role of esterification and alcoholysis agent during the reaction. Therefore, it was determined that for the alcoholysis to be carried out, a solution rich in pentaerythritol must be obtained, thus obtaining oligomers based on PET, such as the BTHNPT.

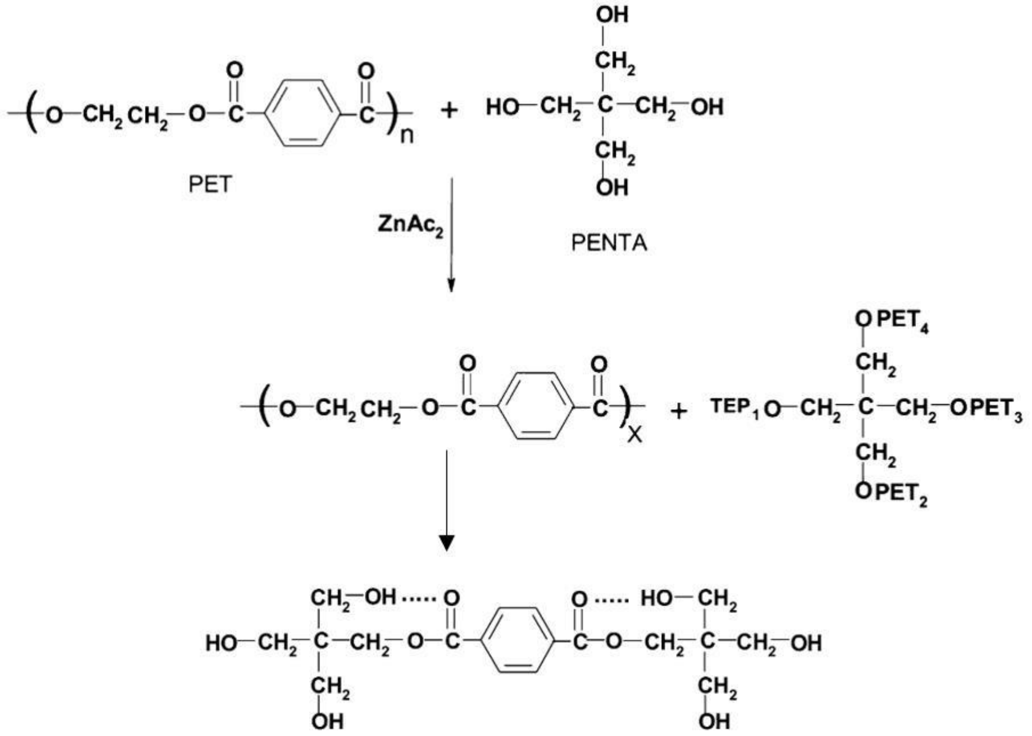


Figure 15. PET depolymerization with pentaerythritol (PENTE) to produce BTHNPT.
Source: Mendes et al., 2011.

Dibutyl terephthalate (DBTP) is a monomer used as adhesives, sealants, and coating products. This depolymerization process uses butanol. S. Liu et al. synthesized DBTP by using butanol in conjunction with different kinds of catalysts such as $ZnCl_2$ and different Brönsted-Lewis ionic acidic liquids (IL). During this reaction a temperature of 205 °C was maintained for 8 hours. The existence of a synergistic effect was determined within the active sites found in the ILs, which improved the conversion of PET, in addition to improving the performance of DBTP. On the other hand, it was determined that [HO3S- (CH2) 3-NEt3] Cl-$ZnCl_2$ was the best catalyst, obtaining a PET conversion of 100% and a DBTP yield of 95.3%. Finally, it was found that the catalyst can be reused up to 7 times without having a significant loss of its catalytic capacity.

PET-Polyols are polyhydric alcohols that have several hydroxyl groups within their structure. Its industrial use is generally in the production of polyurethane. The depolymerization process of PET for the generation of polyols uses ethylene glycol (see Figure 16 for a better description of the reaction mechanism). Scremin et al. performed this procedure by using sodium metasilicate as a catalyst and diethylene glycol. Recycled PET pieces of 5x5 mm were used in 9 different conditions to determine their relationship with the conversion rate. The best conditions for this process were at 210 °C and a reaction time of 5 hours, generated a polyol yield of 58.8%. It was also showed that the sodium metasilicate presented similar results compared to the use of zinc acetate as a catalyst. This catalyst also presented the possibility to be recovered after the reaction, apart from being non-toxic and cheaper. This type of procedure, as in the case of oligomers production, does not have a strong relationship with the alcoholysis process because of the nature of the substance used.

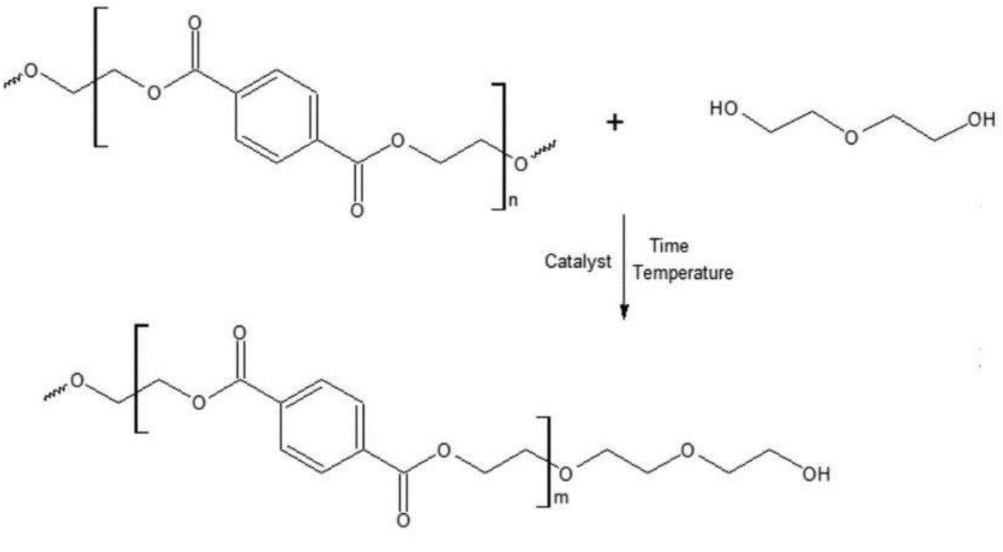


Figure 16. PET depolymerization with pentaerythritol (PENTE) to produce BTHNPT.

Source: Scremin et al., 2011.

Disodium terephthalate (NA_2-TPA) is an organic electrode material which is used in the production of lithium batteries. The obtention of this compound can be realized by different types of alcohols. For this, small amount of HCl is needed. Asakuma et al. established a mechanism of depolymerization of PET using various alcohols such as ethanol, propanol, and hexanol, under atmospheric pressure. The reaction was carried out in a flask at 150–180 °C for 10-120 minutes. For this, virgin PET flakes of 5x5x1 mm were used. Ethanol produced a 30% PET conversion at a temperature of 78 °C for 180 minutes. On the other hand, propanol obtained a conversion close to 83% with a temperature of 97% for 180 minutes. For its part, hexanol generated a conversion close to 84% at a temperature of 150 °C and a time of 12 minutes. It was possible to determine that the smaller alcohol molecules have some advantage in relation to the depolymerization process, obtaining better results in terms of PET conversion and activation energy.

Catalyst effects on the alcoholysis reaction

One of the main objectives of this document is to seek a comparison of the operational aspects involved in the use of catalysts, such as temperature, reaction time and product yield. It was found that there is limited information about the various processes that can be carried out to obtain a specific product. However, it was found that three of the previously studied production processes (DMT, DOTP and DET) had sufficient information to be able to carry out this analysis.

First, it was found that the DMT production process can be carried out under different operating conditions. Figure 17 shows that the reaction time decreases significantly when using a catalyst such as ZnO (Du et al., 2020b), being 93% less than the reaction time of the process carried out without catalyst (Tang et al., 2019), and 87% less than that using supercritical conditions (Q. Liu et al., 2015). Furthermore, Figure 18 shows that the use of catalyst also reduces the operating temperature by 15% compared to the process using no catalyst, and by 43% for the process carried out under supercritical conditions. It is important to clarify that in the case of the process under supercritical conditions, the difference will always be notable due to the conditions that this process presents. Finally, it was found that the process that presented supercritical conditions in the absence of catalyst, presents a higher DMT yield.

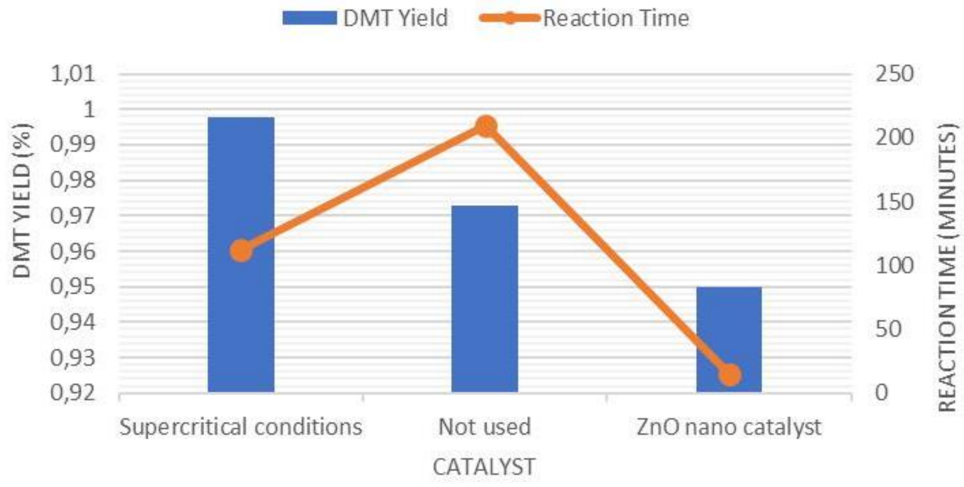


Figure 17. PET depolymerization with pentaerythritol (PENTE) to produce BTHNPT.

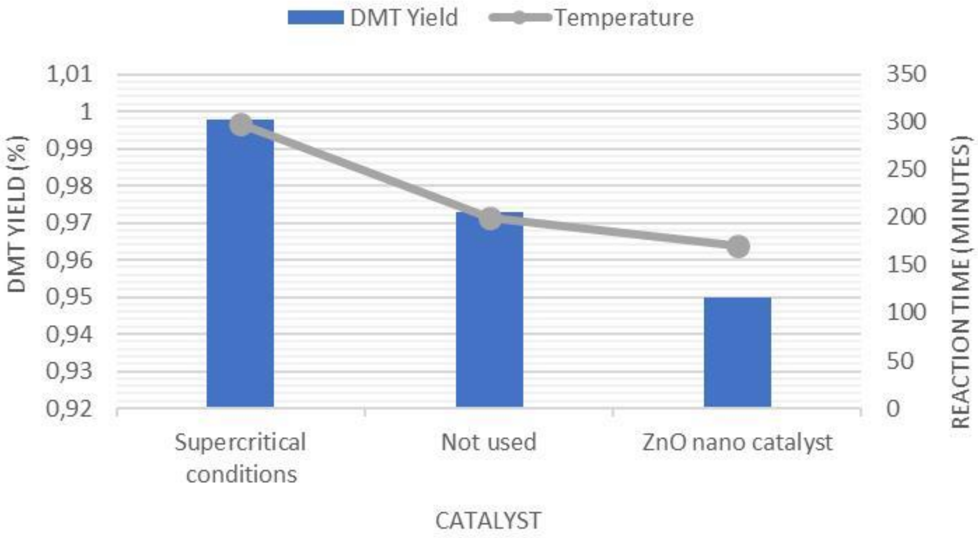


Figure 18. PET depolymerization with pentaerythritol (PENTE) to produce BTHNPT.

Regarding the production of DOTP, it was found that a less constant behavior in terms of the implication that the use of catalysts has on the operating conditions. It can be seen in Figure 19 that the performance of DOTP obtention without catalyst (Liu et al., 2013) is like the one obtained by using ionic liquids (Liu, et al., 2013), but with a difference in reaction time of 63%. Furthermore, if these same parameters are compared with the other reported processes, it is found that the non-use of catalysts could improve the reaction time without impairing the yield of the product. On the other hand, Figure 20 shows that the use of a catalyst can decreases the reaction temperature by 30% in relation to the process that uses ionic liquids. In this case, it is important to note the fact that both the use of zinc acetate (Chen et al., 2014b) and DES (Zhou et al., 2019) show non-competitive results compared to the two other processes.

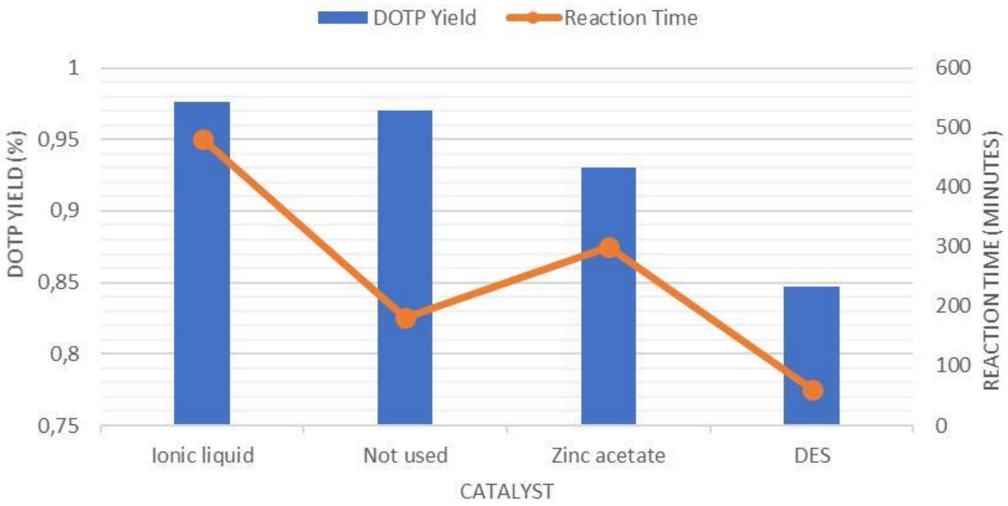


Figure 19. PET depolymerization with pentaerythritol (PENTE) to produce DOTP.

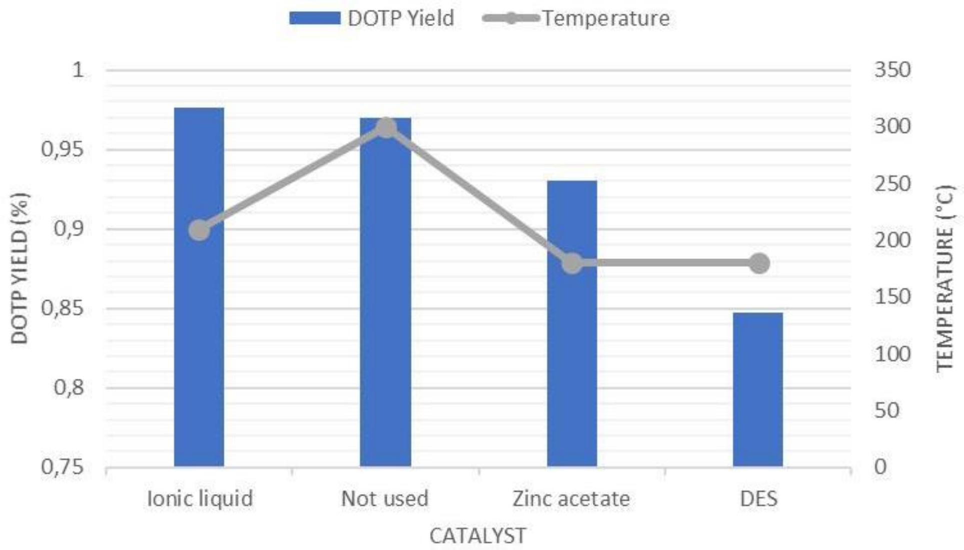


Figure 20. PET depolymerization with pentaerythritol (PENTE) to produce DOTP.

Finally, in the case of DOTP production, a comparison can be observed between the three types of catalysts used. During the analysis of these results (Table 4), it was observed that similar operating conditions were used in the four cases. For the purposes of this comparison, one of the works carried out by Nunes et al., in 2017 was discarded, since it served as a complement to the first work (Nunes et al., 2014). In Figure 21 we see that the main difference of these procedures lies in the reaction time, where the use of [Bmim][BF4] as a catalyst (Nunes et al., 2014) considerably reduces the reaction time by 50 and 63%, compared to the use of Cobalt oxide nanoparticles (Rodrigues et al., 2020) and the use of supercritical conditions without a catalyst (Fávaro et al., 2013).

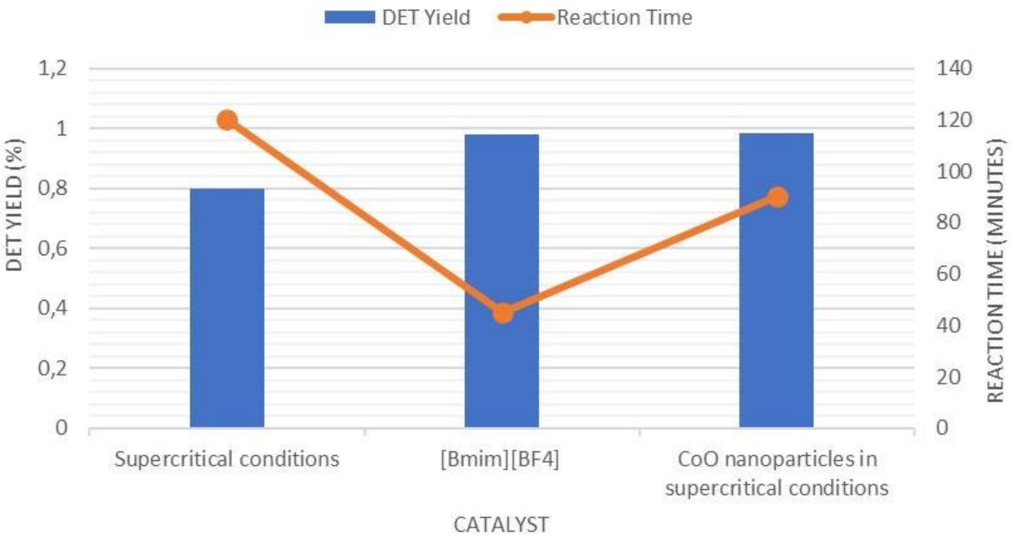


Figure 21. PET depolymerization with pentaerythritol (PENTE) to produce DET.

DISCUSSION

General analysis of the results obtained in the research

The depolymerization of PET via alcoholysis has proven to be a process with great prospects for the future of recycling, this because some of its main disadvantages have been resolved with current research. Implying an improvement for the development of new products, and demonstrating the following characteristics:

1. PET conversion rates and yield of the generated product are almost always within the 90-100% range.

2. The reaction temperature and time can be considerably reduced with the appropriate catalyst.
3. The process for separating a zinc compound catalyst is usually simple since they are insoluble solids in the reaction medium.

On the other hand, it was established that supercritical solvents within PET alcoholysis have great benefits within the established operating conditions, seeing a considerable decrease in reaction time without affecting its performance. However, it is considered that, despite these benefits, the management of supercritical conditions could represent a limitation when it comes to being able to scale this process at an industrial level. Due to its complexity of operation and infrastructure, this type of process can represent higher operating and investment costs. On the other hand, the use of catalysts seems to be a better solution, since this type of reagent allows reducing operating conditions of temperature, pressure, and reaction time, without having to establish new operating conditions. Therefore, the study of new catalysts could be imperative for the future industrial depolymerization of PET via alcoholysis. Within the investigation, the following trends regarding the use of catalysts showed:

1. There is a trend towards the use of zinc-based compounds, such as zinc acetate, zinc chloride, and zinc oxide. This is due to the ease that this type of compound presents when it comes to being separated from the final products.
2. The application of catalysts improves the conversion of PET and the yield of the products by 5-10%. It also decreases the depolymerization temperature by 10-40% and reaction time by 20-90%.
3. The use of ionic liquids (IL) as catalysts presents the possibility of reusing them up to 7 times without losing their properties, maintaining a similar conversion and performance.

4. The use of supercritical conditions can eradicate the need of using a catalyst during the alcoholysis processes.

Within the process of comparing the research articles, a wide inequality was evidenced within the procedures for obtaining DMT, DOTP, and PET Oligomers. This is because these processes were carried out by different types of alcohols and catalysts. In addition, in the processes for obtaining BTHNPT, DBTP, Polyols, and Na_2-TPA, only one result was found for each of the production processes of these compounds. However, some conclusions were obtained:

1. The depolymerization process of PET via alcoholysis presents similar conditions in most cases, which is why the use of alcohol as a reaction solvent turns out to be crucial to obtain a specific product.
2. The degree of purity of alcohol represents an important factor in the yield of the reaction since water could be a limiting agent for the reaction. Therefore, the use of alcohols with concentrations of 99-100% is preferred.
3. The type of PET plastic used, its color, and its particle size appears to be related to factors such as conversion and yield.

Current limitations

The literary review process was limited by the lack of information related to the research and implementation of PET alcoholysis. This, although a total of 1192 results were found, of which only 4% could be used for this work. It is for this reason that the screening had to be carried out individually to determine the applicability of the results obtained within the investigation. On the other hand, sometimes it was difficult to find a clear difference between glycolysis and alcoholysis, as they use similar reagents. Glycol is an organic compound belonging to the group of diols, that is, it has two -OH groups within its structure. In contrast, alcohol is an organic compound that has one -OH group within its structure replacing a hydrogen atom. The difference is theoretically noticeable, however, in practice, this is usually a bit more complicated because both compounds share certain characteristics that make the PET depolymerization process very similar. It is for this reason that during the investigation three scientific articles were found that presented the use of glycols, which were based on partial glycolysis that in these cases was determined as alcoholysis without any scientific support that could revalidate that assumption.

Suggestions for further research

Polyethylene terephthalate is one of the most useful plastic products today. It is mostly used to produce single-use products, generating large amounts of plastic waste every day. Plastic contamination is a really serious problem. New recycling methods must be developed to replace traditional recycling because of its inefficiency. PET alcoholysis seems to be a better option that can easily replace mechanical recycling. This systematic literature review tried to show the latest developments on this important issue, showing all scientific trends present in the production of different products of this depolymerization process, and giving a descriptive overview of the most important operating parameters such as temperature, pressure, and reaction time. Nevertheless, it is suggested to investigate the effects that PET particle size has on conversion and reaction yield. Same study is suggested to be carried out for the catalysts used and establishing investigations that base their research on the industrial and environmental applicability of the various catalysts. Finally, a more in-depth investigation related to the processes of glycolysis and alcoholysis is recommended, facilitating the differentiation that these processes have, because a certain degree of confusion was found during the research.

CONCLUSIONS

The depolymerization process of PET via alcoholysis has shown to have an important advance in recent years. Many of the problems initially presented by this type of chemical recycling have been solved based on the application of new types of catalysts. This has allowed problems such as the yield of the reaction or the difficulty to separate the products and the catalyst have been solved in the best way. It was also found that the use of supercritical conditions can replace the use of catalysts since in some cases they can improve the conversion and the yield of the reaction. On the other hand, a trend towards the use of zinc-based catalysts was found due to their ease of separation within the generated products. In addition, the use of ionic liquids as a catalyst demonstrated high effectiveness and the ability to be reused up to seven times in a row.

It can be concluded that this process still requires research focused on obtaining less common and more innovative products such as polyols or plasticizers. Furthermore, the study and comparison of the effect of different catalysts applied to the same medium are mandatory so that this process can be scaled up at an industrial level. It is also recommended to study the effect that the size of the PET particles have on the reaction. In this systematic literature review, the relevant information was synthesized, focusing on the progress made in these ten years with respect to the PET alcoholysis process. All information has been treated and disclosed in an impartial manner.

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