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Article

Process Analysis of PMMA-Based Dental Resins Scraps Depolimerization: Optimization of Reaction Time and Temperature

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Abstract: In this work, the cross-linked PMMA-based dental resins scraps were submitted to pyrolysis to recover MMA (Methylmethacrylate). The thermal degradation of cross-linked PMMA-based dental resins scraps was analyzed by TG/DTG to guide the operating conditions in pilot scale. The pyrolysis experiments carried out in a reactor of 143L, at 345, 405, and 420°C, 1.0 atmosphere. The reaction liquid products obtained at 345°C, physicochemical characterized for density, kinematic viscosity, and refractive index. The chemical composition of liquid products obtained at 345°C, 30, 40, 50, 60, 70, 80, and 110 minutes, at 405°C, 50, 70, and 130 minutes, and at 420°C, 40, 50, 80, 100, 110, and 130 minutes determined by GC-MS. The experiments show that liquid phase yields were 55.50%, 48.73%, and 48.20% (wt.), at 345, 405, and 420°C, respectively, showing a smooth sigmoid behavior, decreasing with increasing temperature, while that of gas phase were 31.69%, 36.60%, and 40.13% (wt.), respectively, increasing with temperature. The liquid products density, kinematic viscosity, and refractive index obtained at 30, 40, 50, 60, 70, 80, and 110 minutes, varied between 0.9227 and 0.9380 g/mL, 0.566 and 0.588 mm^2/s, and 1.401 and 1.414, respectively, showing percentage deviations between 0.74 and 2.36%, 7.40 and 10.86%, and 0.00 and 0.92%, respectively, compared to standard values for density, kinematic viscosity, and refractive index of pure MMA at 20 °C. The GC-MS identified in the reaction liquid products at 345, 405, and 420°C, 1.0 atm, esters of carboxylic acids, alcohols, ketones, and aromatics, showing concentrations of MMA between 83.454 and 98.975% (area.). For all the depolymerization experiments, the concentrations of MMA in the liquid phase, between 30 and 80 minutes, reach purities above 98% (area.), decreasing drastically with increasing reaction time after 100 minutes, thus making it possible to depolymerize the cross-linked PMMA-based dental resins scraps by pyrolysis to recover MMA. *The optimum operating conditions to achieve high MMA concentrations, as well as elevated yields of liquid reaction products were 345 °C and 80 minutes*.

Keywords: PMMA; Pyrolysis; Plastics Wastes; Depolymerization; Distillation; Recovery of Methylmethacrylate.

1. Introduction

Polymethyl methacrylate (PMMA) is an acrylic polymer (ester of acrylic acid) with superior properties and/or characteristics including high ultraviolet (UV) resistance, high light transmission, optically transparency, good stability, high gloss and hardness (greatest surface hardness among all the thermoplastics), good abrasion resistance, good rigidity, low-medium density (1.17-1.20 g/cm^3), among others [1]. PMMA is one of the most important industrial polymeric materials, widely used in the automobile, construction, furniture, electronics, optical media, mobile communication, cosmetics, medical/dentistry, and until toys industries [1-4]s porous carbonaceous material with reactive, functionalized/aromatic surfaces [1].

PMMA is compatible with human tissue making it an important material for transplants and prosthetics, especially in the field of ophthalmology because of its transparent properties, bio-compatibility, non-toxicity, and absence of tissue irritation (e.g. intraocular lens) [3], as well as in the field of deontology/dentistry because of its good biocompatibility, non-toxicity, color and mechanical stability, non-permeability to body fluids, good aesthetic appearance, absence of taste, odor, and tissue irritation, and particularly teeth adhesion (e.g. bone cement, dental resins, etc.) [4].

World production of PMMA is expected to reach 2.85x10^6 tons by 2020, growing at a compound annual growth rate of 6.1% from 2013 to 2020 [5], and as an environmentally-friend polymer, PMMA is a recyclable material [5-8]. Over the years, plastics wastes were commonly dumped in a landfill or incinerated for energy recovery [8]. However, in the last decades, the global plastics production increased from 10^8 tons in 1989 to 3.35x10^8 tons in 2016 [9], resulting in increased waste streams [8-9]. In 2016, only in Europe, 27.1x10^6 tons of plastic waste were collected, being 31.1% recycled, 41.6% incinerated, and 27.3% land filled [9], posing one of the greatest challenges for disposal and recycling of plastic wastes [8].

Most polymers can be pyrolyzed into hydrocarbons (olefins, aromatic and aliphatic compounds) [6]. However, by pyrolysis of polymethyl methacrylate and polystyrene, the main reaction liquid products are their precursor monomers methyl methacrylate (MMA) and styrene [6-8]. In this context, pyrolysis, one of the most promising process to convert organic polymers of high molecular weight (macromolecules) into smaller fragments [7], has proven to be an alternative means for depolymerization of polymethyl methacrylate (PMMA) into methyl methacrylate (MMA) [6-8], and the literature reports several studies on the subject [6-8, 10-49].

The thermal decomposition of PMMA is a heterogeneous reaction since PMMA is a solid while a gaseous product is formed [12]. By pyrolysis of PMMA, the reaction products include a gas (non-condensable), a liquid (condensable), and a solid phase [6-8, 10-17, 34-35], and until a H_2O phase has been reported [7, 11, 35], probably due to dehydration reactions [18].

The reaction liquid products composed mainly of MMA [6-8, 11-17, 34-35], as well as small concentrations of methyl esters of carboxylic acids (acrylic, propanoic, propionic, isobutyric, and benzoic acids) [7, 11-17, 35], ethyl and butyl esters of carboxylic acids (acrylic acid) [14-15], hydrocarbons (pentene, 2-pentene, cyclopentene, toluene, benzene, propyl benzene, ethyl benzene, etc.) [7, 11-16, 35], alcohols (methanol) [7-8, 11-12, 35], diesters of carboxylic acids (ethylene glycol dimethacrylate) [17], phthalates (phthalic anhydride, dibutylphthalate) [34], ketones (dimethyl cyclopentenone) [35], carboxylic acids (methacrylic acid), among other chemical functions [7, 11-16].

Most studies on the pyrolysis of PMMA have been focused on the reaction mechanism and reaction kinetics by thermo-gravimetric (TG, DTG) [19-24, 26-28, 39, 41, 43-44, 47-48], thermo-gravimetric-Fourier transform infrared spectroscopy (TG/TGA-FTIR) [25-26, 29, 40, 42], differential scanning calorimetry (DSC) [28, 38, 41], differential mass-spectrometric thermal analysis (DMSTA) [43], micro scale combustion calorimetry (MCC) [43, 47], pyrolysis mass spectrometry (DP-MS) [30-31], and flash pyrolysis/analytical pyrolysis (Py–GC/MS) [16, 43, 49]. The progress on reaction mechanism by thermochemical recycling of PMMA described on the excellent review of Moens *et. al.* [50].

PMMA depolymerization performed in fluidized bed reactors [6-8, 11-13, 32, 35, 37], fixed bed reactors [14, 34, 45-46], conical spouted bed reactors [15], and stirred tank batch reactors [16-17], and recently Moens *et. al.* [50] described the progress on reactor technologies for thermal recycling of PMMA [50]. The thermal degradation experiments carried out in micro scale [16, 19-32], bench scale [12, 14, 17], laboratory [8, 11, 13, 15-17, 34-35], and only a few in pilot and/or technical scale [7, 11, 37, 45-46].

Besides the mode of operation of PMMA thermal degradation (fluidized bed reactors, fixed bed reactors, conical spouted bed reactors, and stirred tank batch reactors) [6-8, 11-17, 32, 34-35, 37, 40, 45-46], other factors that affect the chemical composition and yield of reaction liquid products are the characteristics of raw material (pure, filled, and scrap PMMA), reaction temperature, residence time, reaction time, gas flow rate, and the process scale [7-8, 11, 17, 35].

The advantages of thermal degradation of PMMA by pyrolysis include the reduction in the volume of produced gases (non-condensable) [6], the possibility to use low quality PMMA-based materials [6-8, 11, 16-17, 35], and the fact that reaction liquid products are composed mainly of MMA [6-8, 11, 13-17, 34-35, 46]. In addition, the reaction liquid products can be easily purified by distillation to produce high concentrated and/or pure MMA [6-7, 17, 46].

The drawbacks of thermal degradation of PMMA by pyrolysis remains on the fact that PMMA has poor thermal conductivity, degradation of polymeric macromolecules requires considerable amounts of energy, the residence time of monomer vapors in the reactor must be minimized to reduce the formation of degradation products [6-7]. In addition, if high yields are desired, one needs to operate the reactor as a gas-solid fluidized bed, and the operation of gas-solid fluidized reactors with high solid and gas flow rates is complex [35].

In this context, studies analyzed the influence of process parameters on thermal degradation of PMMA by pyrolysis to maximize both the liquid reaction products and the concentration of MMA within the liquid phase [7-8, 11, 17, 35]. The liquid reaction products with relative high concentrations of MMA can be submitted to filtration, as well as decantation, if a H_2O phase is present [7, 11], followed by distillation to obtain pure MMA [17].

Despite some studies focusing the process analysis of PMMA thermal degradation in laboratory, bench, and micro-scale [8, 11-17, 34-35], and pilot or technical scale [6-8, 11, 37, 45-46], *until the moment, no systematic study has investigated the influence of reaction time on the behavior of MMA concentration profile, side reaction products concentrations, and the cumulative mass of reaction liquid products by PMMA depolymerization in pilot scale*. Thermal degradation studies of cross-linked PMMA in semi-pilot and technical scale [16, 37, 46], summarized as follows.

Sasaki and Tsuji [37], investigated the pyrolysis of PMMA to recover MMA using a fluidized bed reactor (φ_{id} = 0.35 m, H = 1.5 m, $V_{Reactor}$ = 144.31 L), containing a second fluidized bed reactor used as separator (φ_{id} = 0.90 m, H = 2.0 m, $V_{Separator}$ = 1272.34 L), in pílot scale. The experiments carried out at 400°C, using homo PMMA with 5.0 mm diameter, at a mass flow rate of 0.004 kg/s, sand with average size of 0.3 mm was used as heating media, at a mass flow rate of 0.04 kg/s, minimum gas fluidization specific velocity of 5.0 cm/s, and mean sand residence times of 2.1 10^3 s, entering in fluidized bed reactor at 580°C. The yield of reaction liquid products was 95.0% (wt.), with an MMA concentration of 95.0% (area.). The MMA within the liquid phase was purified by distillation, reaching concentrations of 99.8% (area.).

Kaminsky and Frank [7], investigated the pyrolysis of PMMA to recover MMA using a fluidized bed reactor (φ_{id} = 154 mm, H = 770 mm, $V_{Reactor}$ = 14.34 L) in laboratory scale. The experiments carried out at 450, 490, and 590°C, using pure PMMA pellets and waste PMMA, at a mass flow rate of 3000 g/h, gas flow of 3.0 m^3/h, and residence times of gas between 0.8 to 1.2 seconds. For the experiments with pure PMMA pellets, the yields of liquid varied between 57.27 and 98.48% (wt.), showing a drastic decrease with temperature, while that of gaseous phase between 1.37 and 42.46% (wt.), showing a sharp increase with temperature. The concentrations of MMA in the liquid phase decreases with temperature, ranging from 54.88 at 590°C to 98.48% (wt.) at 450°C. For the experiment with PMMA waste, the yield of liquid was 92.13% (wt.), with an MMA concentration of 90.99% (wt.). The chemical analysis identified side products including methyl isobutirate, methyl acrylate, among other, whose concentrations increases as the temperature raises.

Kaminsky [6], investigated the pyrolysis of PMMA to recover MMA using a fluidized bed reactor (φ_{id} = 154 mm, H = 770 mm, $V_{Reactor}$ = 14.34 L) in laboratory scale. The experiments carried out at 450°C, using PMMA scraps, at a mass flow rate of 3000 g/h, gas flow of 3.9 m^3/h, residence time of gas 3.2 seconds, and reaction time of 4.0 hours. The yield of liquid reaction products was 96.60% (wt.), while that of gaseous phase 1.25% (wt.), and 0.15% 147(wt.) residue (coke). The concentrations of MMA in the liquid phase achieved 97.20% (wt.).

Kaminsky *et. al.* [8], investigated the pyrolysis of PMMA-ATH, containing 67.0% (wt.) Al_2 $(OH)_3$ and 33.0% (wt.) MMA, and virgin PMMA to recover MMA using a fluidized bed reactor (φ_{id} = 154 mm, H = 770 mm, $V_{Reactor}$ = 14.34 L) in laboratory scale. The experiments carried out at 450°C, at a mass flow rate of 3000 g/h, gas flow of 3.9 m^3/h, residence times of gas 3.2 seconds, reaction time 4.0 hours, and filler(SiO_2)-PMMA(Feed) ratio of 0.75. For the experiments with PMMA-ATH, the yields of liquid products were 24.825% (wt.), while those of H_2O and gaseous phases were 24.40% (wt.) and 0.20% (wt.), respectively, and 50.575% (wt.) residue (coke), from witch 44.00% (wt.) Al_2O_3. The concentration of MMA in the liquid phase was 18.10% (wt.). The GC-MS analysis identified side products including methacrylic acid, methyl propionate, and isobutyric acid. For the experiments with virgin PMMA, the yield of liquid products was 98.02% (wt.), while that of gaseous phases was 1.98% (wt.) and 0.20% (wt.). The concentration of MMA in the liquid phase was 97.20% (wt.). The GC-MS analysis identified traces of side products including methacrylic acid, methyl propionate, isobutyric acid, and methanol.

Kaminsky and Eger [11], investigated the pyrolysis of filled PMMA, containing 62.0 and 71.0% (wt.) SiO_2 and 38.0 and 29.0% (wt.) MMA, respectively, and virgin PMMA pellets to recover MMA using a fluidized bed reactor (φ_{id} = 154 mm, H = 770 mm, $V_{Reactor}$ = 14.34 L) in laboratory scale and in pilot scale. The experiments with filled PMMA carried out at 450°C in laboratory scale, at mass flow rates of 1.9 and 2.0 kg/h, gas flow rates of 3.9 and 5.2 m^3/h, reaction times of 1.0 and 2.9 hours, and residence times of 1.0 and 1.2. The yields of liquid 168phase varied between 96.10 and 96.80% (wt.), relative to the content of organic phase of filled PMMA, while those of gas and solid phases varied between 2.00 and 2.60% (wt.) and 1.20 and 1.30% (wt.), respectively. The concentrations of MMA in the liquid phase varied between 86.60 and 90.50% (wt.) relative to the content of organic phase of filled PMMA. The experiments with virgin PMMA pellets carried out at 450 and 480°C in laboratory scale, at mass flow rates of 0.9 and 1.4 kg/h, gas flow rates of 3.4 and 7.9 m^3/h, reaction times of 1.5 and 4.0 hours, and 174residence times of 0.8 and 1.3. The yields of liquid phase varied between 98.20 and 99.59% (wt.), decreasing with increasing temperature, while those of gas and solid phases between 0.4 and 1.4% (wt.) and 0.01 and 0.40% (wt.), respectively, increasing with increasing temperature. The concentrations of MMA in the liquid phase varied between 93.70 and 98.40% (wt.), decreasing with increasing temperature. The experiments with filled PMMA carried out at 450°C in pilot scale, at a mass flow rate of 34.0 kg/h, gas flow rates of 50.0 m^3/h, reaction times of 11.5 hours, and residence times of 2.9. The yield of liquid phase was 97.20% (wt.), while those of gas and solid phases were 1.60 and 1.20% (wt.), respectively. The concentrations of MMA in the liquid phase was 83.50% (wt.) relative to the content of organic phase. The experiments with virgin PMMA pellets carried out at 450°C in pilot scale, at a mass flow rate of 16.0 kg/h, gas flow rates of 65.0 m^3/h, reaction times of 37.0 hours, and residence times of 1.6. The yield of liquid phase was 99.40% (wt.), while those of gas and solid phases were 0.50 and 0.10% (wt.), respectively. The concentration of MMA in the liquid phase was 96.70% (wt.). For all the experiments, the chemical analysis identified side products including methyl isobutirate, methyl acrylate, methyl propionate, ethyl acrylate, methacrylic acid, and mimethylethylcyclohexene among others.

Smolders and Baeyens [12], investigated the thermal degradation of PMMA Poly(methyl methacrylate) using a fluidized bed in micro scale. The experiments carried out at temperatures between 325 and 525°C using 2.0 g of PMMA. The experimental results show that at low temperatures, the reaction is kinetically controlled, whereas at high temperatures, heat transfer restricted the reaction rate. The MMA-yield is mainly dependent on the residence time of the gas in the reactor and to a lesser extent on the operating temperature.

Kang *et. al.* [13], investigated the thermal degradation kinetics of virgin PMMA copolymer and PMMA waste using a fluidized bed reactor in laboratory scale. The experiments carried out at 440, 450, 460, 470, 480, and 500°C, using virgin PMMA and waste PMMA, at a mass flow rates between 190 and 310 g/h, residence times of gas average 0.5 seconds, and gas flow rate between 29 and 31 NL/min. For the experiments with virgin PMMA, the yields of liquid varied between 98.10 and 99.30% (wt.), showing a smooth decrease with temperature, while that of gaseous phase lies between 0.5 and 1.80% (wt.), showing an increase with temperature. The concentrations of MMA in the liquid phase decreases smoothly with temperature, ranging from 97.34 at 440°C to 96.30% (wt.) at 470°C. For the experiments with PMMA wastes, the yields of liquid varied between 96.80 and 98.40% (wt.), while that of gaseous phase lies between 1.5 and 3.10% (wt.). The concentrations of MMA in the liquid phase decreases smoothly with temperature, ranging from 95.65 to 97.29% (wt.). The chemical analysis identified side products including methyl isobutirate, ethyl acrylate, butyl acrylate, and benzene among others. In addition, the boiling point of distillation was just above 100°C, meaning that MMA ($T_{Boiling} = 101°C$) was the main component of liquid phase products with more than 96.0% (wt.). The mass balance of all the experiments shows that the total yield of common comonomers (MMA, MA and EA) ranged from 97 to 98% (wt.) for virgin PMMA, and from 95 to 97% (wt.) for PMMA waste.

Dimitris S. Achilias [14], investigated the pyrolysis of virgin PMMA to recover MMA using a bench scale fixed bed reactor ($\varphi_{id} = 12.5$ mm, H = 121 mm, $V_{Reactor} = 14.85$ mL). The experiments carried out at 450°C, using 1.5 g of PPMA, reaction times of 17 minutes. The yield of liquid phase was 99.30% (wt.), while those of gas and solid phases were 0.60 and 0.10% (wt.), respectively. The concentration of MMA in the liquid phase was 99.0% (wt.). The chemical analysis identified side products including methyl propionate, propanoic acid, 2-methyl-, methyl ester, propanoic acid, 2,2-dimethyl-, methyl ester among others.

Lopez *et. al.* [15], investigated the pyrolysis of virgin PMMA to recover MMA using a continuous bench scale conical spouted bed reactor ($H_{Cilinder} = 34$ cm, $H_{Cone} = 20.5$ cm, $D_{Cilinder} = 6.15$ cm, $D_{Cone} = 2.0$ cm, $V_{Reactor} = 2569.5$ mL). The experiments carried out at 400, 450, 500, and 550°C, mass flow rate of 1.5 g/min, reaction time of 10 minutes. The yields of liquid phase varied between 90.81 and 99.14% (wt.), decreasing with increasing temperature, while that of gaseous phase lies between 0.86 and 9.19% (wt.), increasing with increasing temperature. The concentrations of MMA in the liquid phase decrease with temperature, ranging from 77.86 to 86.50% (wt.). The chemical analysis identified side products including methyl propionate, propanoic acid, 2-methyl-, methyl ester, 2-butenoic acid methyl ester, propanoic acid, 2,2-dimethyl-, methyl ester among others.

Szabo *et. al.* [16], investigated the thermal degradation of PMMA-ABS wastes, containing 69.0% (wt.) PPMA and 31.0% (wt.) ABS, respectively, to recover MMA using a stirred batch reactor ($V_{Reactor} = 5.0$ L) in semi-pilot scale. The experiments carried out at 500°C, using 500 g PMMA-ABS wastes, under N_2 atmosphere, and reaction time of 75 minutes. The yields of liquid, gas and solid phase products were 65.0, 31.8 and 3.2% (wt.), respectively. The concentration of MMA in the liquid phase was 21.50% (wt.), while that of styrene was 15.39% (wt.). The density, kinematic viscosity, and calorific value of liquid phase products were 0.945 g/cm^3, 2.3 mm^2/s (20°C), and 34.08 MJ/kg, respectively. The chemical analysis identified large amounts of side products, approximately 63.11% (area.), including acrylonitrile, propanoic acid methyl ester, methyl isobutyl ester, toluene, ethylbenzene, alpha-methylstyrene, 4-phenylbutylnitrile, 4-phenyl-2 methylbutanoic acid, 1,3-diphenyl-propane, among others.

Braido *et. al*. [17], investigated the pyrolysis of homopolymer PMMA and cross-linked PMMA-based dental resins scraps at 250, 300, 350, 400, and 450°C, reaction times of 60, 90, and 120 minutes, in a laboratory scale glass reactor (φ_{id} = 30.0 mm, H = 150 mm, $V_{Reactor}$ = 106 mL), as well as using cross-linked PMMA-based dental resins scraps at 400°C, reaction times of 60 minutes, in a semi-pilot scale stainless steel reactor (φ_{id} = 80.0 mm, H = 400 mm, $V_{Reactor}$ = 2000 mL). The experiments in laboratory scale carried out with 20 g homopolymer PMMA and PMMA-based dental resins scraps. For the experiment in laboratory scale with homopolymer PMMA and PMMA-based dental resins scraps, the yields of liquid phases varied approximately between 9.0 and 89.0% (wt.), increasing with temperature until 400°C, whereas it becomes almost constant between 400 and 450°C, while those of solids varied approximately between 1.0 and 88.0% (wt.), decreasing exponentially with temperature until 400°C, whereas it becomes almost constant between 400 and 450°C. The concentrations of MMA in the liquid phase varied between 82.2 and 99.9% (wt.). For the experiment in semi-pilot scale with PMMA-based dental resins scraps, the yields of liquid, solid, and gas phases were 66.3, 26.3 and 7.4% 256(wt.), respectively, being the monomer (MMA) recovery 76.4% (wt.). The chemical analysis by GC-MS identified in the liquid products obtained with PMMA-based dental resins scraps 258side products including MMA dimer, methyl benzoate, and ethylene glycol dimethacrylate.

Bisi *et. al.* [46], investigated the pyrolysis of cross-linked PMMA-based dental resins scraps at 345°C, 1.0 atm, using pilot scale fixed bed tubular reactor of 143 L. The yield of liquid reaction products was 55.50% (wt.). The GC-MS, identified in the reaction liquid products, esters of carboxylic acids, alcohols, ketones, and aromatics. The concentrations of MMA in the liquid phase, between 30 and 80 minutes, reach purities higher than 98% (Area), decreasing drastically with increasing the reaction time after 100 min.

This work aims to evaluate the effect of temperature by the pyrolysis cross-linked PMMA-based dental resins scraps, using a reactor of 143 L, at 345, 405, and 420°C, and 1.0 atmosphere, on the yield of reaction liquid products and MMA (Methylmethacrylate) concentration of liquid phase, and to optimize the recovery of MMA. In addition, this study has systematically investigated the influence of reaction time on the behavior of MMA concentration profile, side reaction products concentration profile, and the cumulative mass of reaction liquid products by PMMA depolymerization in pilot scale. The liquid phase subjected to fractional distillation in a laboratory scale column (Vigreux) at 105°C, according to the boiling temperature of MMA, in order to obtain fractions not only with high concentration of MMA, but also with similar physicochemical properties (density, kinematic viscosity, and refraction index). Finally, the morphology of cross-linked PPMA-based dental resins scraps and the solid phase (coke) after pyrolysis at 345ºC and 1.0 atmosphere analyzed by scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX).

2. Materials and Methods

2.1. Methodology

The process flow sheet shown in Figure 1 summarizes the applied methodology, described in a logical sequence of ideas, chemical methods, and procedure to produce MMA (Methylmethacrylate) by fractional distillation of liquid phase reaction products produced by thermal degradation (pyrolysis) of cross-linked PMMA-based dental resins scraps at 345, 405, and 450 °C and 1.0 atmosphere, in pilot scale. Initially, the mass, longitudinal and transversal diameter of PMMA-based dental resins scraps determined (biometry). Afterwards, thermal gravimetric analysis of PMMA-based dental resins scraps carried out to guide the experiments in pilot scale. The pyrolysis carry out to investigate the influence of process temperature and reaction time on yield of liquid phase and concentration of MMA within the liquid phase products. The liquid phase reaction products submitted to fractional distillation to produce MMA with high purity. The physical-chemistry properties and chemical composition of distillation fractions were determined. The solid phase characterized by MEV and EDS.

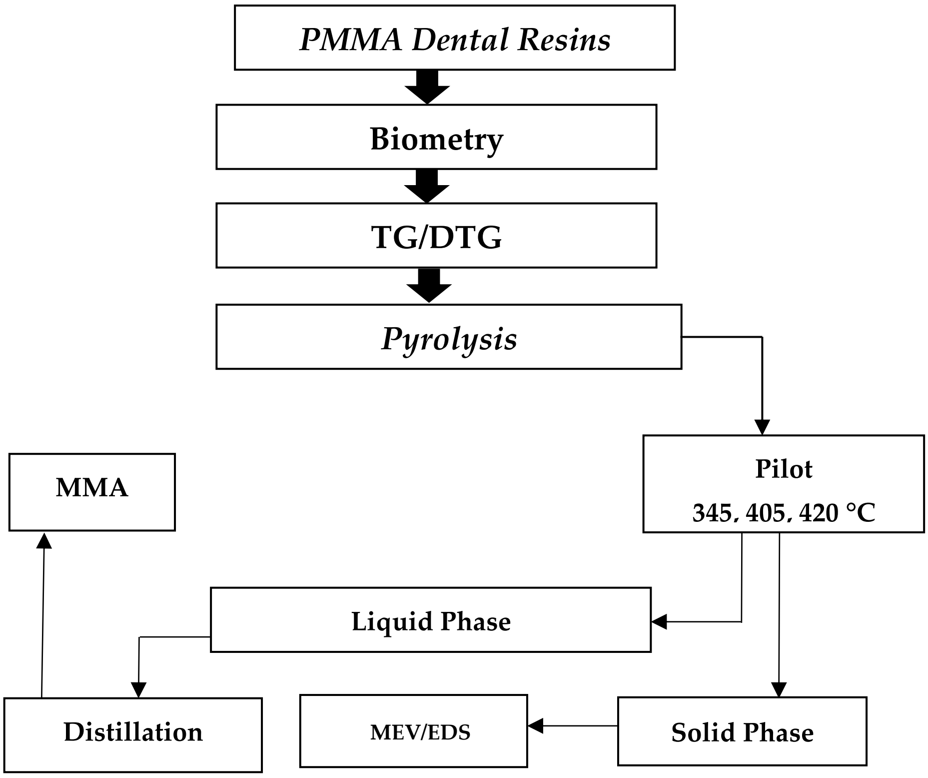

Figure 1. Process flow sheet by the production of high purity MMA by fractional distillation of liquid phase reaction products obtained by thermal degradation of cross-linked PMMA-based dental resins in pilot scale.

2.2. *Materials*

The cross-linked PMMA-based dental resin scraps, illustrated in Figure 2, provided by Dentsply Indústria e Comércio Ltda (Petrópolis, Rio de Janeiro, Brazil). The PPMA-based dental resin scraps contain 1.0% (wt.) inert color spreaders (TiO_2) and 5.0% (wt.) of cross-linking agent EGDMA (ethylene glycol dimethacrylate) [17].

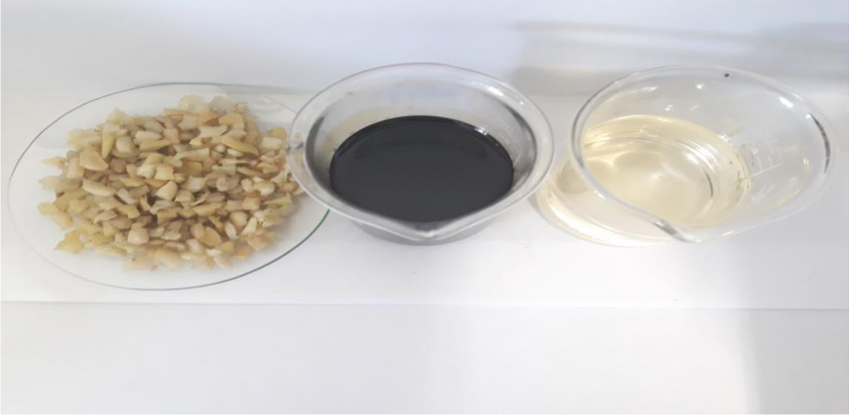

Figure 2: Cross-linked PMMA-based dental resins scraps, liquid reaction products (Dark Liquid) obtained after pyrolysis at 345, 405, and 420°C, 1.0 atmosphere, in pilot scale, and MMA (Colorless Liquid) obtained by fractional distillation of liquid reaction products.

2.3. *Biometry of cross linked PMMA-based dental resins*

The cross-linked PPMA-based dental resin scraps chosen ran domically, weighed using a semi-analytical balance (Marte Balanças e Aparelhos de Precisão Ltda, Brazil, Model: AL200C) and the horizontal and vertical diameters determined using a digital caliper micrometer (India Machine Tools and Hardware, India, Model: DANIU 150 mm), being the average vertical and longitudinal diameters and mass defined by Eqs (1), (2), and (3), as follows.

$$\emptyset_{M,T} = \frac{\sum_{i=1}^{n} d_{i,T}}{n} \tag{1}$$

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$$\emptyset_{M,L} = \frac{\sum_{i=1}^{n} d_{i,L}}{n} \tag{2}$$

$$M_M = \frac{\sum_{i=1}^{n} m_i}{n} \tag{3}$$

Where, $d_{i,T}$, $d_{i,L}$, m_i and are the transversal and longitudinal diameters, and mass of the i-th particle, and $\emptyset_{M,T}$, $\emptyset_{M,L}$, and M_M are the average transversal and longitudinal diameters, and mass of particles agglomerate.

2.4. Thermogravimetric (TG) analysis of cross-linked PMMA-based dental resin scraps

The TG/DTG analysis of cross-linked PMMA-based dental resins scraps described in details elsewhere [46].

2.5. Pyrolysis of PMMA

2.5.1. Experimental apparatus and procedures

The apparatus, used for the pyrolysis experiments, illustrated in Figure 3. The apparatus is described in detail elsewhere [51-54], operates in batch mode at 345, 405, and 420°C and 1.0 atmosphere, under air atmosphere, using pieces of cross-linked PMMA-based dental resins scraps as raw material. The experimental procedures described elsewhere [46, 54].

Figure 3: Experimental apparatus (Thermal Catalytic Cracking Unit) for the pyrolysis of cross-linked PMMA-based dental resins scraps at 345, 405, and 420°C, 1.0 atmosphere, in pilot scale.

2.6. Fractional distillation of liquid phase reaction products

The fractional distillation of reaction liquid products performed by using an experimental apparatus (Vigreux borosilicate-glass distillation column), described in detail elsewhere [51-53], as shown in Figure 4. The distillation carried out at 105°C ($T_{\text{Boiling,MMA}}$ = 101 °C) [46]. The mass of distillates weighed and physicochemical characterized for density, kinematic viscosity, and refractive index, as described in section 2.7.1.

Figure 4: Vigreux borosilicate-glass distillation column of 500 ml, connecting column, condenser, and separator funnel.

2.7. Physical-Chemistry Analysis and Chemical Composition of Bio-Oils and Distillation Fractions

2.7.1. Physical-Chemistry Analysis of Distillation Fractions

The distillation fractions, obtained according to the boiling temperature range of methyl methacrylate (MMA), physicochemical characterized for density (ASTM D4052) at 25°C, kinematic viscosity (ASTM D445/D446) at 40°C, and refractive index (AOCS Cc 7-25), as described in the literature [46, 51-53].

2.7.2. GC-MS of reaction liquid products

The separation and identification of all the chemical compounds present in the reaction liquid phase performed by CG-MS as described in details elsewhere [46, 54].

2.8. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) of cross-linked PMMA-based dental resins scraps

The morphology of cross-linked PMMA-based dental resins scraps and the solid phase products (coke) obtained after pyrolysis at 420°C and 1.0 atm, in pilot scale, performed by scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX) using a scanning electron microscope (FEI company, USA, Model: Quanta 250 FEG), coupled to chemical analysis detector EDS, using carbon pin stubs specimen, and a high vacuum sputter coater (Leica, Germany, Model: EM ACE600), using a deposition film of gold.

2.9. Material balance by pyrolysis of cross-linked PMMA-based dental resins scraps

Application of mass conservation principle in the form an overall steady state mass balance within the stirred tank reactor, operating in batch mode, closed thermodynamic system, yields the following equations.

$$\sum_i M_{i,In} = \sum_j M_{j,Out} \qquad (4)$$

$$M_{Reactor} = M_{Feed} \qquad (5)$$

$$M_{Reactor} = M_{SP} + M_{LP} + M_{Gas} \qquad (6)$$

Where $M_{i,In}$ is the mass of i-th stream entering the reactor, $M_{j,Out}$ is the mass of j-th stream leaving the reactor, $M_{Feed} = M_{PMMA}$ is the mass of cross-linked PMMA-based dental resins scraps, M_{SP} is the mass of solid phase (coke), M_{LP} is the mass of reaction liquid products.

3. Results

3.1. Biometry of cross-linked PMMA-based dental resin scraps

Table 1 shows the biometry of cross-linked PMMA-based dental resins scraps particles aggregate. The average mass of particle aggregate was 100.00 ± 47.70 mg, while the average $\emptyset_{M,T}$ transversal and $\emptyset_{M,L}$ longitudinal diameters were 5.94 ± 1.49 and 8.69 ± 1.83 mm, respectively, much higher than the particles sizes and/or diameters $\emptyset_{Particle}$ of PMMA raw materials (PMMA, PMMA-ATH, PMMA-SiO_2, and PPMA-Granite) reported in the literature by Kaminsky and Franck ($\emptyset_{Particle}$ of 0.5-1.5 mm) [7], by Kaminsky and Eger ($\emptyset_{Particle}$ of 0.01–0.1 mm and 0.1–1.0 mm) [11], by Smolders and Baeyens ($\emptyset_{Particle}$ of 0.5-1.0 mm) [12], by Kang *et. al.* ($\emptyset_{Particle}$ of 1.0–1.5 mm) [13], and Braido *et. al.* ($\emptyset_{Particle}$ of 0.2 mm) [17], and of the same order than the particles sizes and/or diameters of Kaminsky *et. al.* ($\emptyset_{Particle}$ of 2-4 mm) [8], Lopez *et. al.* ($\emptyset_{Particle}$ of 3.0 x 4.0 mm) [15], Braido *et. al.* ($\emptyset_{Particle}$ of 1.0-10.0 mm) [17], and Popescu *et. al.* ($\emptyset_{Particle}$ of 5.0-15.0 mm) [34].

Table 1: Biometry of cross-linked PMMA-based dental resins scraps, average particle transversal $\emptyset_{M,T}$ and longitudinal $\emptyset_{M,L}$ diameters and M_M mass, maximum particle transversal $\emptyset_{Max,T}$ and $\emptyset_{Max,L}$ longitudinal diameters and M_{Max} mass, minimum particle transversal $\emptyset_{Min,L}$ and $\emptyset_{Min,L}$ longitudinal diameters and M_{Min} mass, of particles aggregate, and $\emptyset_{Particle}$ particle sizes of virgin and filled PPMA reported in the literature [7-8, 11-13, 15, 17, 34-35].

Biometry	A_V	σ	σ^2	[7]	[8]	[11]	[12]	[13]	[15]	[17]	[34]	[35]
$\emptyset_{M,T}$ [mm]	5.94	1.49	2.23									
$\emptyset_{Max,T}$ [mm]	9.80											
$\emptyset_{Min,T}$ [mm]	3.10											
$\emptyset_{M,L}$ [mm]	8.69	1.83	3.34									
$\emptyset_{Max,L}$ [mm]	12.2											
$\emptyset_{Min,L}$ [mm]	5.90											
M_M [mg]	100	47.7	2.27									
M_{Max} [mg]	231											
M_{Min} [mg]	41											
$\emptyset_{Particle}$ [mm]	-	-	-	0.5-0.15	2-4	0.01–0.1, 0.1–1.0	0.5-1.0	1.0-1.5	4.0 x 3.0	0.2, 1-10	5-15	0.1-0.6

A_{Value} = Average; σ = Standard Deviation; σ^2 = Variance.

3.2. *Thermogravimetric (TG/DTG) analysis of cross-linked PMMA-based dental resin scraps*

To analyze the thermal decomposition behavior and/or characteristics of cross-linked PMMA-based dental resin scraps, the TG/DTG technique was applied, in order to better guide the experimental conditions. Figure 5 shows the thermogravimetry (TG) and derivative thermogravimetry (DTG) analysis of cross-linked PMMA-based dental resin scraps. As one observes, the cross-linked PMMA-based dental resin scraps are thermally stable between 25°C and 200°C. The thermal degradation of cross-linked PMMA-based dental resin scraps starts around 200°C, losing approximately 5.0% (wt.) mass at 300°C, 40.0% (wt.) mass at 350°C, 90.0% (wt.) mass at 405°C, 95.0% (wt.) mass at 420°C, and 100.0% (wt.) mass at 420°C, showing a thermal degradation behavior similar to that reported by Braido *et. al.* [17], for parings PMMA. As reported elsewhere [19, 21], by thermal degradation of PMMA under oxygen containing atmosphere (O_2, Air), a complex oxidation process takes place [19]. In addition, thermal degradation of PMMA under oxygen containing atmosphere (O_2, Air) causes an increase on the PMMA thermal stability by increasing between 50°C and 70°C, the temperature for initiation of mass loss [19, 21]. However, above 230°C, gas-phase oxygen containing atmosphere (O_2, Air) destabilizes the PMMA, causing an acceleration of the thermal degradation process [19, 21]. Hirata *et. al.* [19] and Peterson *et.*

al. [21], reported by thermal degradation of virgin PMMA under oxygen containing atmosphere (O_2, Air), that a mass loss of approximately 90.0% (wt.) occurs at 350°C, while at 400°C PMMA has been completely decomposed. By the fact that the experimental apparatus described in section 2.4.1, operates under air atmosphere, the pyrolysis temperature was set at 345°C, to minimize the energy consumption of LPG.

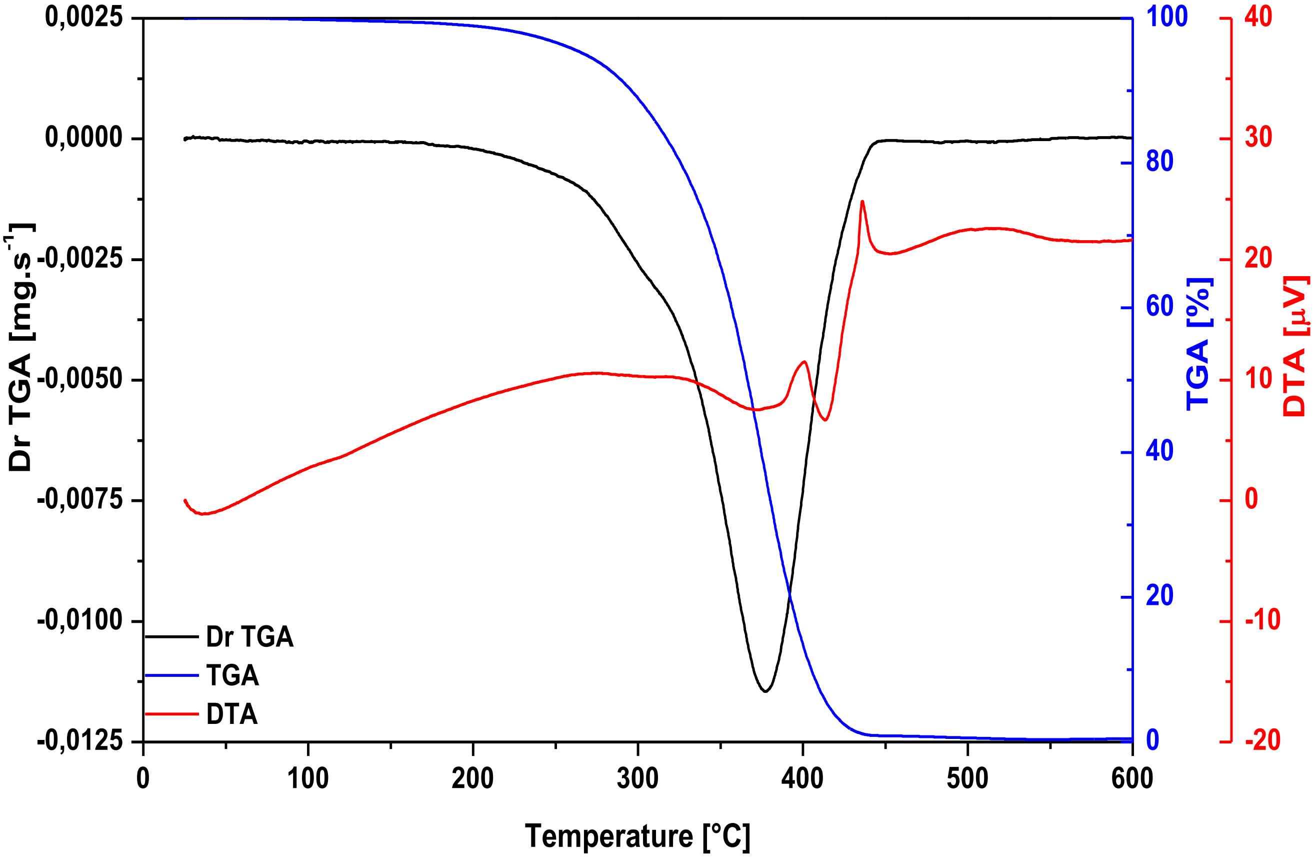

Figure 5: Thermogravimetric (TG/DTG) analysis of cross-linked PMMA-based dental resin scraps.

3.3. *Pyrolysis of cross-linked PMMA-based dental resins scraps*

3.3.1 *Process conditions, material balances, and yields of reaction products by pyrolysis of cross-linked PMMA-based dental resins scraps*

The process conditions, material balances, and yields of reaction products (solid, liquid, and gas) after pyrolysis of cross-linked PMMA-based dental resins scraps at 345, 405, and 420°C, reaction times of 125 and 140 minutes, using a pilot scale stirred tank reactor of 143 L are illustrated in Table 2 and Figure 6.

Table 2: Process parameters and overall steady state material balances by thermal degradation of cross-linked PMMA-based dental resins scraps at 345, 405, and 420°C, 1.0 atmosphere.

Process Parameters	Cracking Temperature [°C]		
	345	405	420
Mass of Dental Resins [kg]	14.60	15.00	15.00
Mass of GLP [kg]	7.00	6.35	7.65
Thermal Cracking Time [min]	125	140	140
Mechanical Stirrer Speed [rpm]	0	0	0
Initial Temperature of Liquid Condensation [°C]	68	63	83
Initial Temperature of Gas Production [°C]	85	80	102
Final Cracking Temperature [°C]	345	405	420
Mass of Solids [kg]	1.87	2.20	1.75
Mass of Liquids [kg]	8.10	7.31	7.23
Mass of Gas [kg]	4.63	5.49	6.02
Yield of Liquids [kg]	55.50	48.73	48.20
Yield of Solids [kg]	12.81	14.67	11.67
Yield of Gas [kg]	31.69	36.60	40.13

The experimental data shows liquid phase yields ranging from 48.20 to 55.50% (wt.), solid phase yields between 11.67 and 14.67% (wt.), and gas yields between 31.69 and 40.13% (wt.). The liquid phase yield decreases with process temperature in a sigmoid fashion, while that of gas phase increases in the same fashion. The same sigmoid behavior for both liquid and gaseous phases, as a function of temperature, was observed by plotting both liquid and gaseous phase yields reported by Kaminsky and Frank [7], as shown in Figure 5. The liquid phase yields are smaller but close to those reported by Szabo *et. al.* (65.0%) [16] and Braido *et. al.* (66.30%) [17], who used the same raw material (cross-linked PMMA-based dental resins scraps) and an apparatus like that described in section 2.4.1 [17], smaller than those reported by Kaminsky (96.60%) [6], Kaminsky and Frank (92.13%) [7], Kang *et. al.* (96.80 and 98.40%) [13], and Popescu *et. al.* (90.0%) [34], and higher than those reported by Kaminsky *et. al.* (24.825%) [8], Kaminsky and Eger (27.87-28.07%) [11], and Grause *et. al.* (18.0-31.0%) [35], for the thermal degradation of filled PMMA and PMMA wastes [6-8, 11, 13, 16-17, 34-35]. The liquid phase yields are smaller than those reported in the literature [6-7, 13], probably due not only to the mode of operation [6-7], but also to the smaller particle sizes ($\emptyset_{Particle}$) used [7, 11, 13, 35], as illustrated in Table 1. Since PMMA has a poor thermal conductivity [6], the larger the particle size ($\emptyset_{Particle}$), the worse the heat transfer, and the lower the conversion of PMMA into MMA, and hence the liquid phase yield.

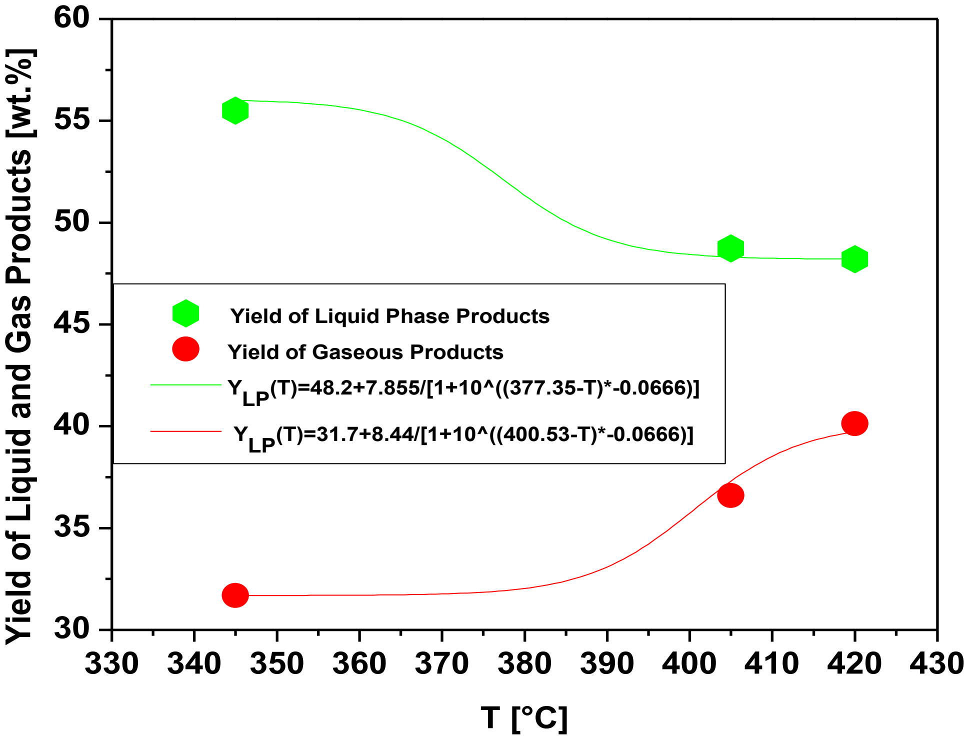

Figure 6: Yield of liquid and gaseous phase products by pyrolysis of cross-linked PMMA-based dental resins scraps at 345, 405, and 420°C and 1.0 atmosphere.

According to Table 4, MMA concentrations up to 98.97% (area.) could be achieved in the liquid phase at 345°C, 1.0 atmosphere, and 30 minutes, higher than those reported by Kaminsky and Frank (97.20%) [6], Kaminsky and Frank (90.99%) [7], Kaminsky *et. al.* (18.10%) [8], Kaminsky and Eger (86.60-90.50%) [11], Kang *et. al.* (95.65-97.29%) [13], Szabo *et. al.* (21.50%) [16], Braido *et. al.* (82.20-95.40%) [17], and Grause *et. al.* (53.0-69.0%) [35]. In addition, the only side products identified by GC-MS in the liquid reaction products obtained by pyrolysis cross-linked PMMA-based dental resins scraps at 345°C, 1.0 atmosphere, and 30, 40, 50, 60, 70, and 80 minutes, were methyl isobutyrate and ethylene glycol dimethacrylate, showing that no side reactions have taken place, compared to several side products reaction reported in the literature [7-8, 11, 13-17, 34-35], corroborating to assert that thermal degradation of PMMA should be carried at reaction times up to and/or around 80 minutes. This is probably to the fact that high residence times, as well as high operating temperatures of monomer vapors inside the reactor contributes to the formation of degradation products [6-7].

3.3.2 *Kinetics of cross-linked PMMA-based dental resins scraps thermal degradation*

The kinetics of cross-linked PMMA-based dental resins scraps thermal degradation at 345°C, reaction times of 125 minutes, using a pilot scale stirred tank reactor of 143 L are illustrated in Figure 7, 8, and 9. The cumulative mass of reaction liquid products illustrated in Figure 7 shows a first order kinetic behavior, that is, the cumulative mass of reaction liquid products increases exponentially with a root mean square error of 0.99, showing a maximum between 90-100 minutes. The exponential first order function validates the assumption of a first order kinetics, being according to the kinetic of PMMA depolymerization reaction reported by Smolders and Baeyens [12] and Lopez *et. al.* [15], except by the fact that both used 2.0 g and 15.0 g feed, respectively. In fact, until the moment, no study reported in the literature, the kinetic of cumulative mass during the thermal degradation process of PMMA by pyrolysis in pilot scale.

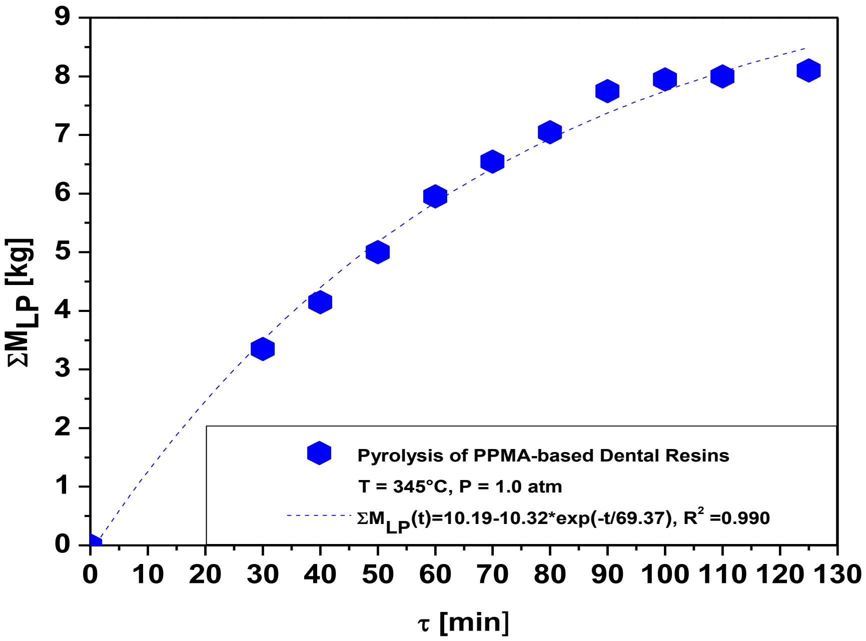

Figure 7: Cumulative mass of reaction liquid products obtained by pyrolysis of PMMA-based dental Resins scraps at 345°C and 1.0 atmosphere.

The cumulative yield of reaction liquid products illustrated in Figure 8, increases exponentially with a root mean square error (r^2) of 0.98, showing a maximum between 90-100 minutes, remaining almost constant between 100 and 130 minutes. In addition, the MMA concentration between 80 and 110 minutes, illustrated in Figure 10, decreases drastically from 97.76% to 88.00% (wt.), showing that reaction time should not exceed 80-90 minutes. This is probably related to high residence times and operating temperatures of monomer vapors inside the reactor, contributing to the formation of degradation products [6-7].

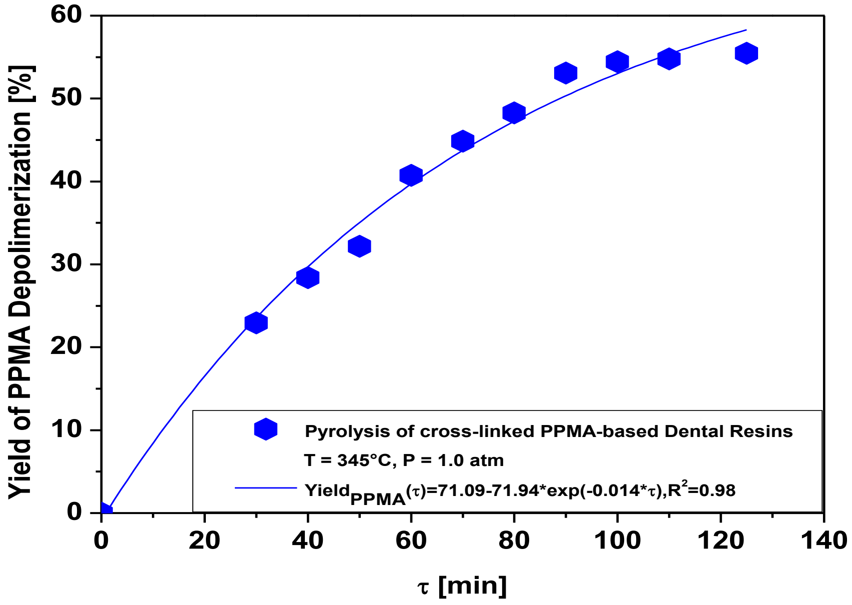

Figure 8: Cumulative yield of reaction liquid products (PMMA Depolymerization) by pyrolysis of PMMA-based dental resins scraps at 345°C and 1.0 atmosphere.

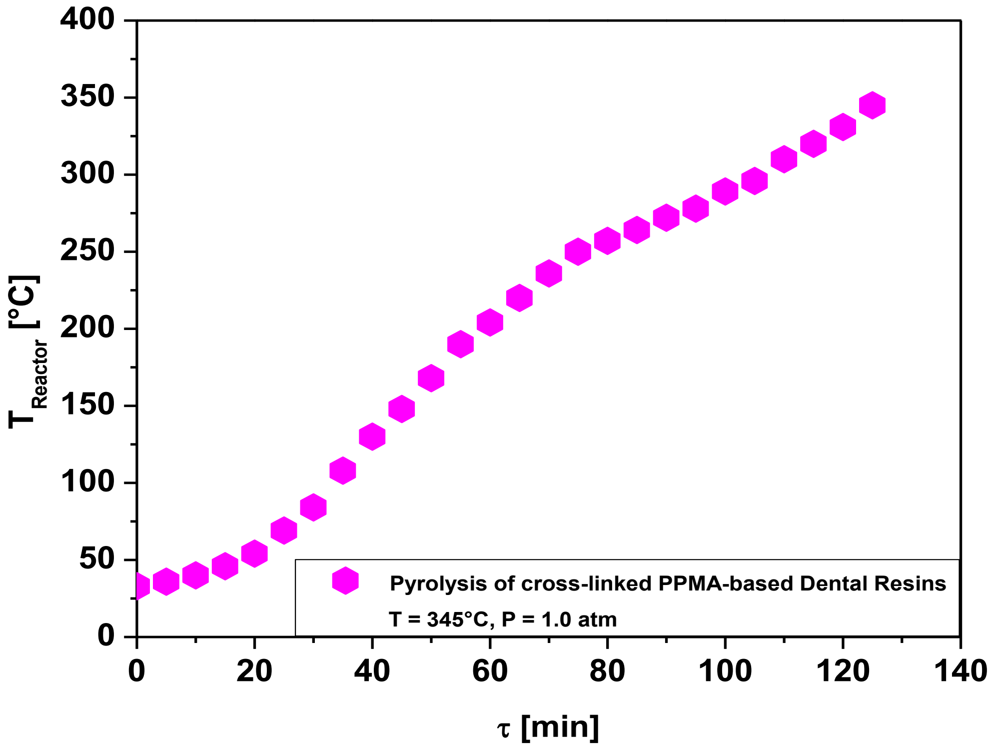

Figure 9: Course of reactor temperature by pyrolysis of cross-linked PMMA-based dental resins scraps at 345°C and 1.0 atmosphere.

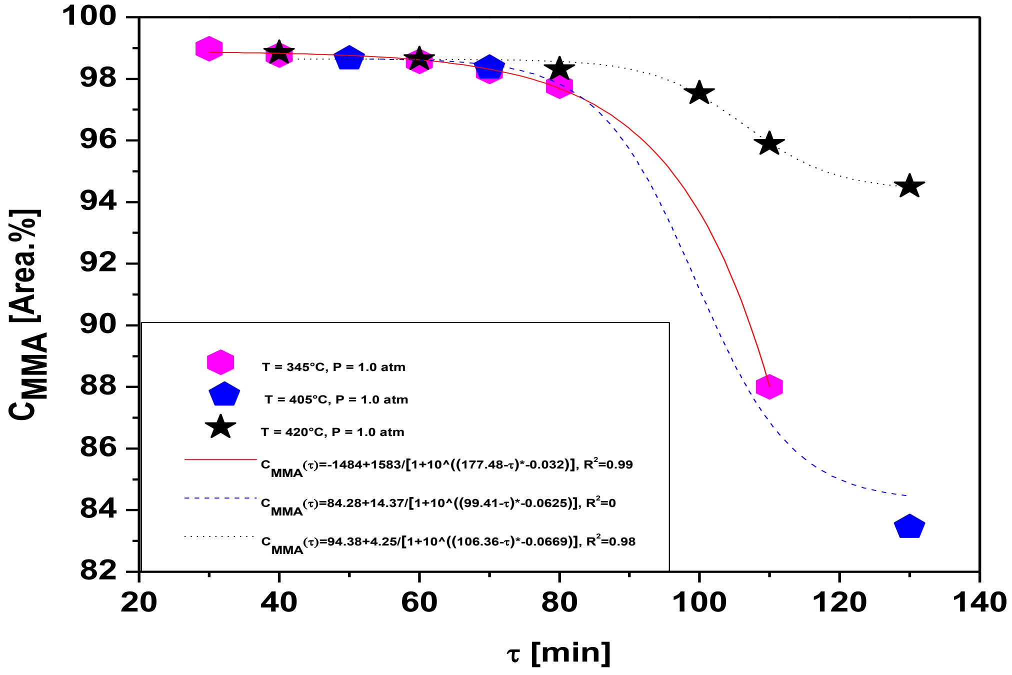

Figure 10: Concentration profile of methyl methacrylate (MMA) by pyrolysis of cross-linked PMMA-based dental resins scraps at 345°C, 30, 40, 50, 60, 70, 80, and 110 minutes, 405°C, 50, 70, and 130 minutes, and at 420°C, 40, 50, 80, 100, 110, and 130 minutes, and 1.0 atmosphere.

Figure 9 shows that course of reactor temperature by pyrolysis of cross-linked PMMA-based dental resins scraps at 345°C and 1.0 atmosphere. Between 0 and 90 minutes, the temperature inside the reactor grows almost exponentially, whereas between 90 and

130 minutes, it grows linearly. In addition, between 80 and 100 minutes, reactor temperature varies between 250 and 275°C. Because both cumulative mass and reaction liquid products yields show a maximum between 90-100 minutes, the optimal operating reactor temperature could be set at 275°C, thus saving energy to thermally degrades PMMA into MMA.

3.4. *Physicochemical analysis of distillation fractions*

Table 3 presents the physico-chemical characterization of distillation fractions of reaction liquid products obtained by thermal degradation of cross-linked PMMA-based dental resins scraps at 345 °C, 1.0 atmosphere, and 30, 40, 50, 60, 70, 80, 110 minutes. The density of distillation fractions, measured at 30 °C, varied between 0.9227 and 0.9380 g/cm^3, showing deviations between 0.74 and 2.36%, compared to the density of pure MMA at 20 °C. The densities are lower, but according to that reported by Szabo *et. al.* [16], of 0.945 g/cm^3. The kinematic viscosity, measured at 40 °C, varied between 0.566 and 0.588 mm^2/s, showing deviations between 7.40 and 10.86%, compared to the kinematic viscosity of pure MMA at 20°C. The kinematic viscosities are lower than that reported by Szabo *et. al.* [16], of 1.90 mm^2/s, measured at 40°C, for PMMA-ABS thermal degradation. Finally, the refractive index, measured at 30°C, varied between 1.401 and 1.414, showing deviations between 0.00 and 0.92%, compared to the refractive index of pure MMA at 20 °C. The results presented in Table 3 show lower values for the densities and kinematic viscosities, compared to those of pure MMA at 20 °C, as illustrated in Table 2, because the physico-chemical properties were measured at 30 and 40 °C, respectively, and the kinematic viscosity of MMA decreases with temperature [16].

Table 3: Physico-chemical characterization of distillation fractions of reaction liquid products obtained by thermal degradation of cross-linked PMMA-based dental resins scraps at 345°C, 1.0 atmosphere, and 30, 40, 50, 60, 70, 80, 110 minutes.

Physicochemical Properties	Cracking Temperature [°C]							
	345							
	Time [min]							
	30	40	50	60	70	80	110	References
ϱ [g/mL], 30 °C	0.9312	0.9299	0.9320	0.9380	0.9227	0.9240	0.926	0.945 (20 °C)
Refractive Index [-],30 °C	1.404	1.411	1.401	1.409	1.414	1.405	1.401	1.414-1.416 (20 °C)
μ [cSt], 40 °C	0.574	0.569	0.588	0.576	0.568	0.570	0.566	0.635 cSt (20 °C)

3.5. *Chemical analysis of liquid reaction products*

3.5.1. *Kinetics of chemical composition profile of MMA in the liquid reaction products*

Tables 4, 5, and 6 illustrate the classes of compounds, summation of peak areas, CAS numbers, and retention times of chemical compounds identified by CG-MS of liquid reaction products obtained by pyrolysis of cross-linked PMMA-based dental resins scraps at 345°C, 1.0 atmosphere, and 30, 40, 50, 60, 70, 80, 110 minutes, at 405°C, 1.0 atmosphere, and 50, 70, 130 minutes, and at 420°C, 1.0 atmosphere, and 40, 50, 80, 100, 110, 130 minutes. The chemical compositions presented in Tables 4, 5, and 6, were plotted in Figure 10 to analyze the influence of process temperature and reaction time on the concentration of MMA within the liquid reaction products.

Table 4: Classes of compounds, summation of peak areas, CAS number, and retention times of chemical compounds identified by CG-MS of liquid reaction products obtained by pyrolysis of cross-linked PMMA-based dental resins scraps at 345°C, 1.0 atmosphere, and 30, 40, 50, 60, 70, 80, and 110 minutes.

doi:10.20944/preprints202110.0097.v1

τ [min]	Class of Chemical Compounds	RT [min]	CAS	ω_i (Area.%)
30	**Esters of Carboxylic Acids**			
	Methyl isobutyrate	3.319	547-63-7	1.02
	Methyl methacrylate	3.676	80-62-6	98.98
	Σ (Area.%) =			**100.00**
40	**Esters of Carboxylic Acids**			
	Methyl isobutyrate	3.322	547-63-7	1.22
	Methyl methacrylate	3.669	80-62-6	98.78
	Σ (Area.%) =			**100.00**
50	**Esters of Carboxylic Acids**			
	Methyl isobutyrate	3.321	547-63-7	1.25
	Methyl methacrylate	3.670	80-62-6	97.15
	Ethylene glycol dimethacrylate	14.004	97-90-5	1.60
	Σ (Area.%) =			**100.00**
60	**Esters of Carboxylic Acids**			
	Methyl isobutyrate	3.320	547-63-7	1.43
	Methyl methacrylate	3.668	80-62-6	98.57
	Σ (Area.%) =			**100.00**
70	**Esters of Carboxylic Acids**			
	Methyl isobutyrate	3.320	547-63-7	1.76
	Methyl methacrylate	3.678	80-62-6	98.24
	Σ (Area.%) =			**100.00**
80	**Esters of Carboxylic Acids**			
	Methyl isobutyrate	3.318	547-63-7	2.24
	Methyl methacrylate	3.668	80-62-6	97.76
	Σ (Area.%) =			**100.00**
110	**Esters of Carboxylic Acids**			
	Methyl isobutyrate	3.314	547-63-7	3.56
	Methyl methacrylate	3.664	80-62-6	88.00
	Butanoic acid, 2-methyl-, methyl ester	4.717	868-57-5	1.83
	Σ (Area.%) =			**93.39**
	Aromatics			
	Toluene	4.560	108-88-3	2.32
	Σ (Area.%) =			**2.32**
	Alcohols			
	Mesitol	12.458	527-60-6	2.18
	Σ (Area.%) =			**2.18**
	Ketones			
	Platambin-1,6-dione	18.495	58556-83-5	2.11
	Σ (Area.%) =			**2.11**

By analyzing the concentration profile of MMA in the liquid reaction products with reaction times, one observes that high concentrations of MMA are achieved at the beginning of monomer vapors condensation around 30 minutes, decreasing with reaction time in a smooth fashion up to 80 minutes, whereas a drastic decrease on the concentration of MMA occurs between 80 and 130 minutes for the thermal degradation of cross-linked PMMA-based dental resins scraps at 345°C and 405°C, corroborating to assert that reaction time should not exceed 80-90 minutes. However, one has not observed the same behavior for the thermal degradation of cross-linked PMMA-based dental resins scraps at 420°C, whereas a decrease on the concentration of MMA occurs, but not drastic, between 80 and 130 minutes.

Table 5: Classes of compounds, summation of peak areas, CAS number, and retention times of chemical compounds identified by CG-MS of liquid reaction products obtained by pyrolysis of cross-linked PMMA-based dental resins scraps at 405°C, 1.0 atmosphere, and 50, 70, and 130 minutes.

τ [min]	Class of Chemical Compounds	RT [min]	CAS	ω_i (Area.%)
50	**Esters of Carboxylic Acids**			
	Methyl isobutyrate	3.319	547-63-7	1.34
	Methyl methacrylate	3.667	80-62-6	98.66
	Σ (Area.%) =			**100.00**
70	**Esters of Carboxylic Acids**			
	Methyl isobutyrate	3.318	547-63-7	1.64
	Methyl methacrylate	3.666	80-62-6	98.36
	Σ (Area.%) =			**100.00**
130	**Esters of Carboxylic Acids**			
	Methyl isobutyrate	3.322	547-63-7	1.52
	Methyl methacrylate	3.668	80-62-6	83.45
	Benzoic acid, methyl ester	10.610	93-58-3	2.60
	2-Propenoic acid, 2-methyl-, 1,2-ethanediyl ester	14.003	97-90-5	3.28
	Hexanedioic acid, 2-methyl-5-methylene-, dimethyl ester	14.226	4513-62-6	3.08
	Σ (Area.%) =			**93.93**
	Alcohols			
	Mesitol	12.459	527-60-6	2.35
	Σ (Area.%) =			**2.35**
	Ketones			
	Platambin-1,6-dione	18.494	58556-83-5	3.72
	Σ (Area.%) =			**3.72**

Figure 11 illustrates the GC-MS of reaction liquid products after pyrolysis of cross-linked PMMA-based dental resins scraps at 345°C, 1.0 atmosphere, and 30 minutes. As described in Table 4, only 02 (two) chemical compounds were identified, MMA (Methyl methacrylate) with a concentration of 98.975% (area.) and methyl isobutyrate with a concentration of 1.025% (area.), showing that pyrolysis of cross-linked PMMA-based dental resins scraps at 345°C, 1.0 atmosphere, and 30 minutes, produced MMA of high purity, and hence, large amounts of cross-linked PMMA-based dental resins scraps could be recovered.

Table 6: Classes of compounds, summation of peak areas, CAS number, and retention times of chemical compounds identified by CG-MS of liquid reaction products obtained by pyrolysis of

cross-linked PMMA-based dental resins scraps at 420°C, 1.0 atmosphere, and 40, 50, 80, 100, 110, and 130 minutes.

τ [min]	Class of Chemical Compounds	RT [min]	CAS	ω_i (Area.%)
40	**Esters of Carboxylic Acids**			
	Methyl isobutyrate	3.319	547-63-7	1.15
	Methyl methacrylate	3.668	80-62-6	98.85
	Σ (Area.%) =			**100.00**
50	**Esters of Carboxylic Acids**			
	Methyl isobutyrate	3.319	547-63-7	1.36
	Methyl methacrylate	3.667	80-62-6	98.64
	Σ (Area.%) =			**100.00**
80	**Esters of Carboxylic Acids**			
	Methyl isobutyrate	3.318	547-63-7	1.68
	Methyl methacrylate	3.666	80-62-6	98.32
	Σ (Area.%) =			**100.00**
100	**Esters of Carboxylic Acids**			
	Methyl isobutyrate	3.317	547-63-7	2.46
	Methyl methacrylate	3.665	80-62-6	97.54
	Σ (Area.%) =			**100.00**
110	**Esters of Carboxylic Acids**			
	Methyl isobutyrate	3.318	547-63-7	2.06
	Methyl methacrylate	3.668	80-62-6	95.89
	Σ (Area.%) =			**97.95**
	Ketones			
	Platambin-1,6-dione	18.498	58556-83-5	2.05
	Σ (Area.%) =			**2.05**
130	**Esters of Carboxylic Acids**			
	Methyl isobutyrate	3.317	547-63-7	2.67
	Methyl methacrylate	3.664	80-62-6	94.51
	Σ (Area.%) =			**97.18**
	Ketones			
	Platambin-1,6-dione	18.494	58556-83-5	2.82
	Σ (Area.%) =			**2.82**

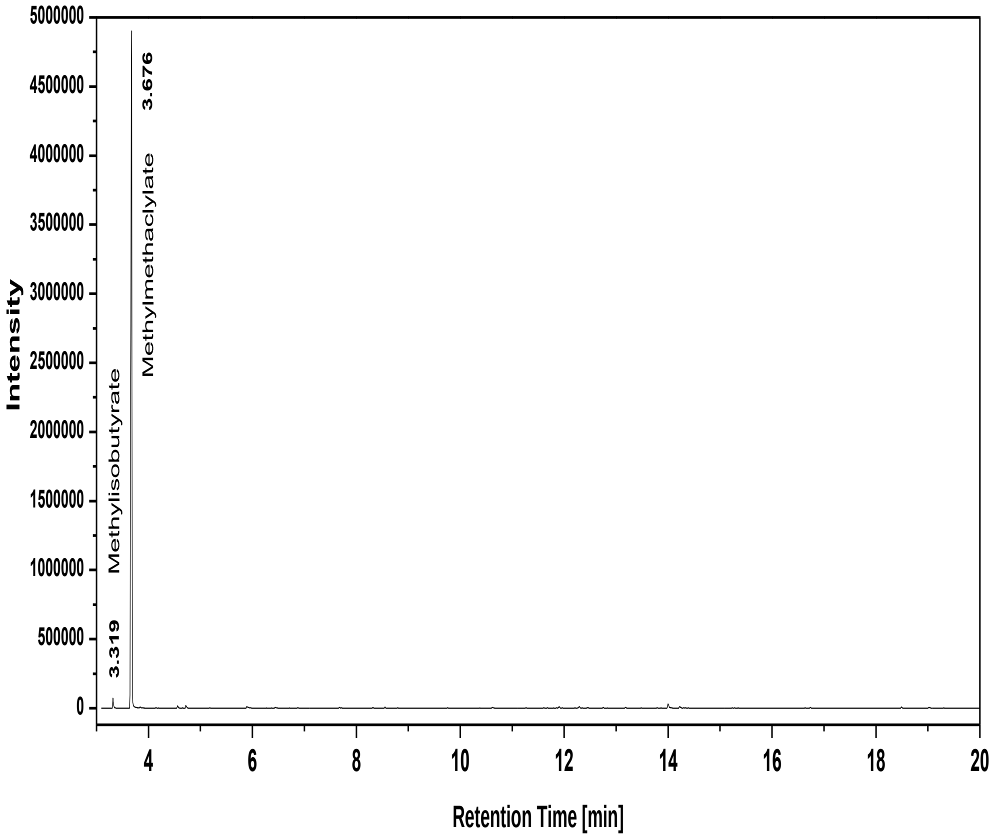

Figure 11: GC-MS of reaction liquid products after pyrolysis of cross-linked PMMA-based dental resins scraps at 345°C, 1.0 atmosphere, and 30 minutes.

3.5.2. Influence of reaction time on reaction side products (methyl isobutyrate)

The concentration profile of methyl iso-butyrate, a side reaction product, as a function of reaction time by pyrolysis of cross-linked PMMA-based dental resins scraps at 345°C, 1.0 atmosphere, 30, 40, 50, 60, 70, 80, and 110 minutes is shown in Figure 12. It can be observed that concentration of methyl iso-butyrate increases with reaction time in a sigmoid fashion, reaching around 3.75% (area.) at 110 minutes. This is probably due to high residence times and operating temperatures of monomer vapors inside the reactor, thus, contributing to the formation of degradation products [6-7]. In fact, others side reaction products including esters of carboxylic acids (1.827%), aromatics (2.320%), alcohols (2.179%), and ketones (2.109) have been identified by CG-MS, totalizing 11.997% (area.). The formation of side reaction products by thermal degradation of virgin PMMA, filled PMMA, and waste PMMA has been reported extensively in the literature [7-8, 11, 13-17, 34-35].

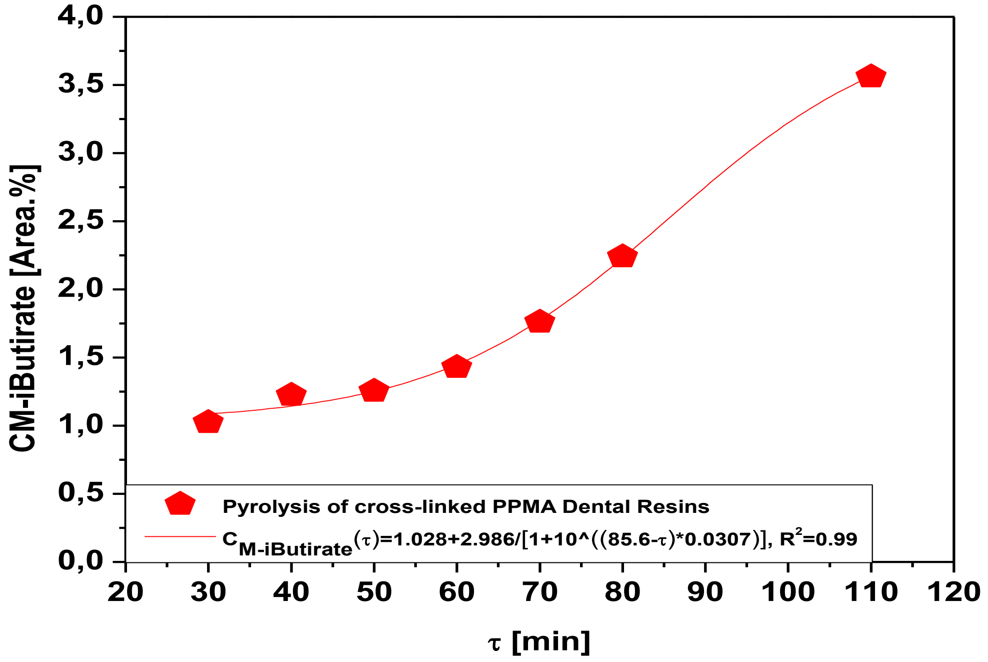

Figure 12: Concentration profile of methyl iso-butyrate, a side reaction product, by pyrolysis of cross-linked PMMA-based dental resins scraps at 345°C, 1.0 atmosphere, 30, 40, 50, 60, 70, 80, and 110 minutes.

3.5.3. Influence of reaction temperature on reaction side products (methyl isobutyrate)

Figure 13 shows the concentration profile of methyl iso-butyrate, a side reaction product, by pyrolysis of cross-linked PMMA-based dental resins scraps at 345, 405, and 420°C, 1.0 atmosphere, and 50 minutes.

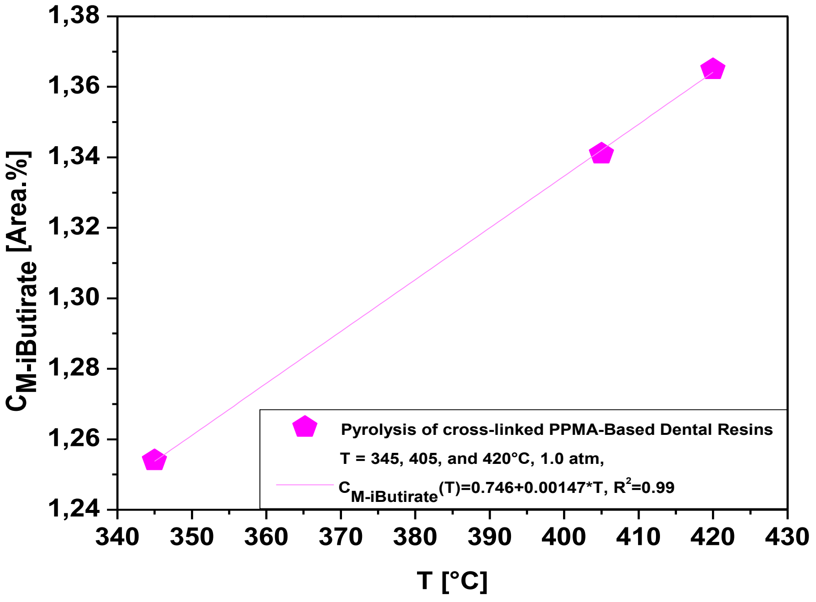

Figure 13: Concentration profile of methyl iso-butyrate, a side reaction product, by pyrolysis of cross-linked PMMA-based dental resins scraps at 345, 405, and 420°C, 1.0 atmosphere, and 50 minutes.

The concentration of methyl iso-butyrate increases linearly with increasing process temperature, being according to the results reported by Kaminsky and Frank [7], who reported that concentrations of methyl iso-butyrate, methyl acrylate, and methyl propionate increase with increasing temperature. The sum of concentrations of methyl iso-butyrate, methyl acrylate, and methyl propionate were 0.40, 0.48, and 1.59% (wt.), respectively, at 450, 490, and 590°C, showing that higher temperatures favors the formation of side reaction products.

3.6. Morphology of cross-linked PMMA-based dental resins scraps

3.6.1. SEM analysis of cross-linked PMMA-based dental resins scraps

The scanning electron microscopies of cross-linked PMMA-based dental resins scraps before and after pyrolysis at 420°C and 1.0 atmosphere are shown in Figures 14 and 15, respectively. SEM was applied to investigate changes on the polymer surface structure during the pyrolysis process.

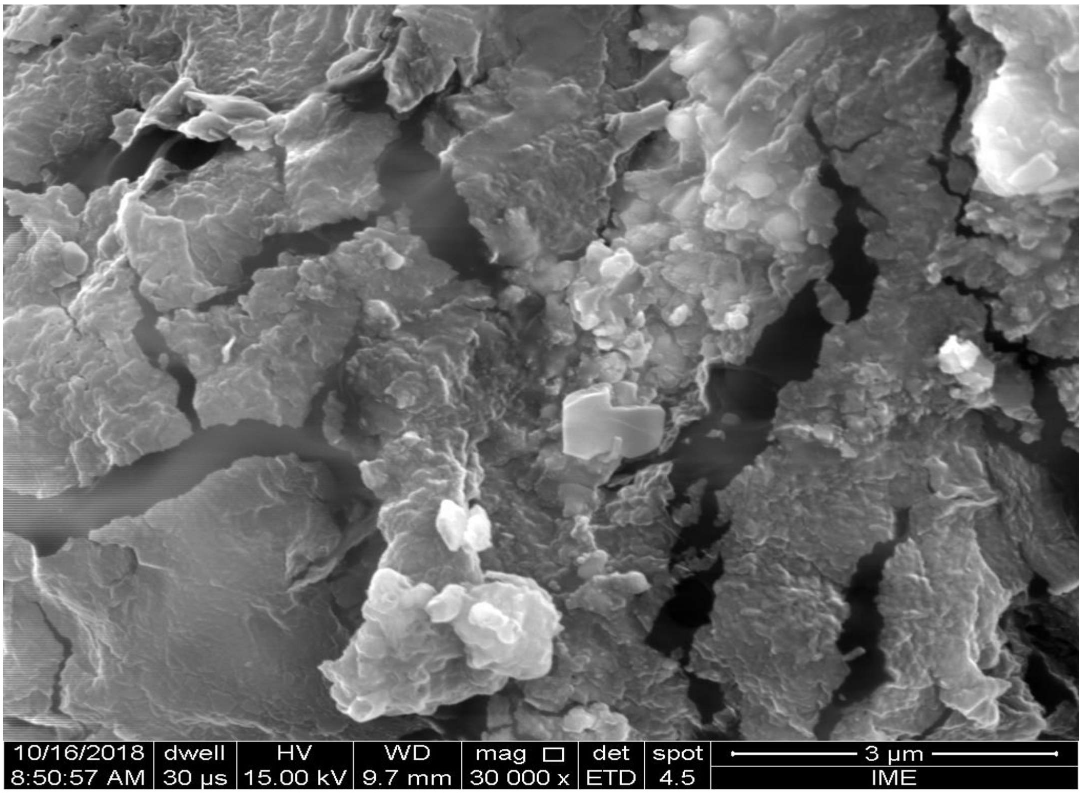

Figure 14: Scanning electron microscopy (SEM) of cross-linked PMMA-based dental resins scraps (MAG: x30000).

By comparison of SEM images of cross-linked PMMA-based dental resins scraps before and after pyrolysis, it can be observed for cross-linked PMMA-based dental resins scraps that an aggregate and heterogeneous structure with irregular shapes, and until the presence of cavities, dominates within the polymer, as shown in Figure 14, while the pyrolysis process had a drastic effect on the polymer morphology, as the polymer surface structure differs largely from its original microscopic characteristics, as observed in Figure 15, as all the polymeric material is carbonized, producing a homogeneous, uniform, and smooth surface without cavities. In addition, according to Table 7, the cross-linked PMMA-based dental resins scraps after pyrolysis at 345°C and 1.0 atmosphere, contains only carbon, showing that thermal degradation of cross-linked PMMA-based dental resins scraps temperature has caused substantial and/or drastic changes on the morphological structure of polymer by degrading $(CH_2{=}C(CH_3)COOCH_3)n$ into $(CH_2{=}C(CH_3)COOCH_3)$.

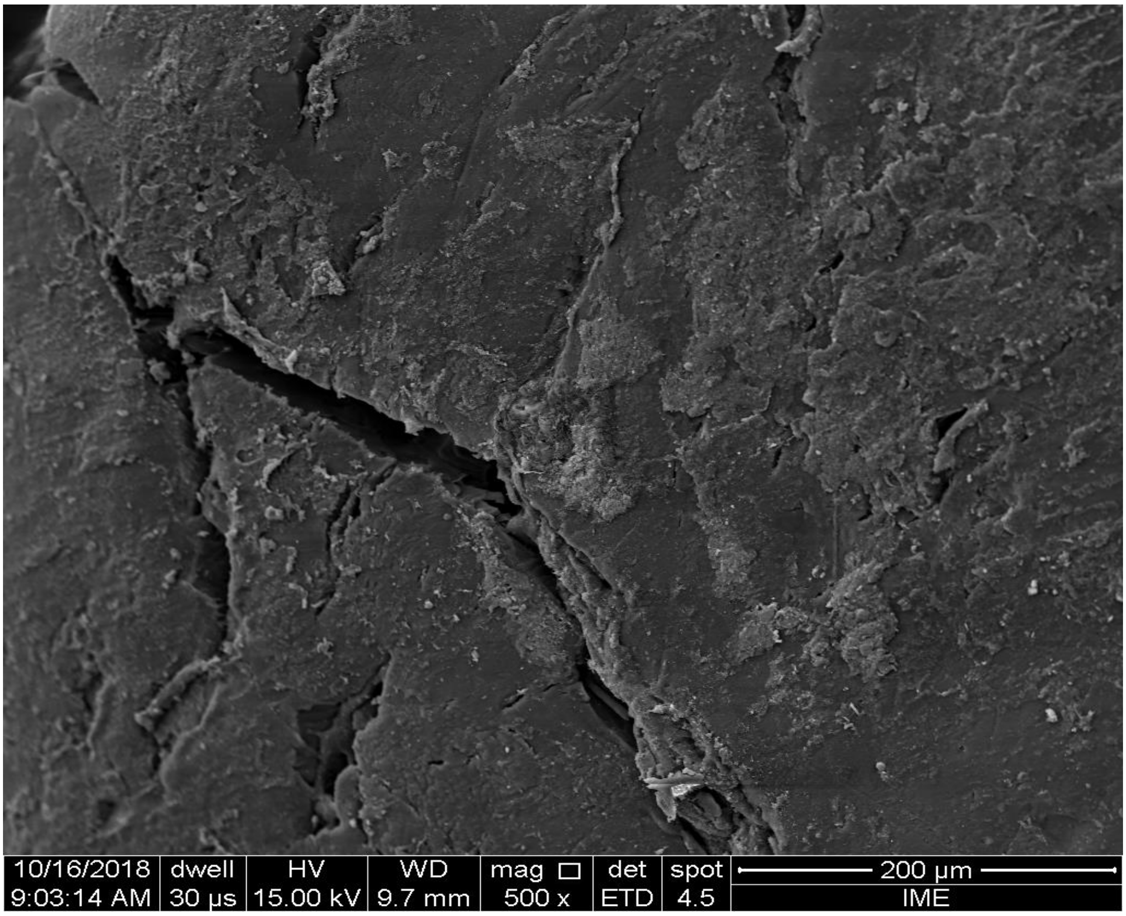

Figure 15: Scanning electron microscopy of cross-linked PMMA-based dental resins scraps after pyrolysis at 345, 1.0 atmosphere, and 130 minutes (MAG: x500).

3.6.2. *EDX analysis of cross-linked PPMA-based dental resins scraps*

Table 7 illustrates the energy dispersive X-ray (EDX) spectroscopy of cross-linked PMMA-based dental resins scraps before and after pyrolysis at 345°C and 1.0 atmosphere.

Table 7: Percentages in mass and atomic mass of cross-linked PMMA-based dental resins scraps before and after pyrolysis at 345°C and 1.0 atmosphere by EDX technique.

	345°C, 1.0 atmosphere			PMMA-based Dental Resins Scraps		
Chemical Elements	Mass [wt.%]	Atomic Mass [wt.%]	SD	Mass [wt.%]	Atomic Mass [wt.%]	SD
Au	**-**	**-**	**-**	60.10	16.10	3.03
Cu	-	-	-	13.59	11.29	0.67
C	**100.00**	**100.00**	**0.00**	**12.81**	**56.30**	**2.99**
Zn	-	-	-	4.63	3.74	0.27
Ti	**-**	**-**	**-**	**4.21**	**4.64**	**0.23**
Ni	-	-	-	2.48	2.23	0.16
O	-	-	-	1.54	5.09	0.52
Fe	-	-	-	0.63	0.59	0.07

SD= Standard Deviation.

The results show that after pyrolysis, cross-linked PMMA-based dental resins scraps becomes a carbonaceous material with a carbon content of 100% (wt.), while that of cross-linked PMMA-based dental resins scraps before pyrolysis shows the presence of Au, Cu, Zn, Ni, and Fe, chemical elements present in gold alloys, used as a deposition film to cover the cross-linked PMMA-based dental resins scraps samples, as well as C, O, and Ti, chemical elements present in the chemical formulas of PMMA ($CH_2=C(CH_3)COOCH_3$)n, ethylene glycol dimethacrylate ($C_{10}H_{14}O_4$), and Titan(IV)-oxide (TiO2), according to the composition of cross-linked PMMA-based dental resins scraps reported by Braido *et. al.* [17].

4. Conclusions

Because by thermal degradation of virgin PMMA under oxygen containing atmosphere (O_2, Air), a mass loss of approximately 90.0% (wt.) occurs at 350 °C [19, 21], the pyrolysis temperature was set at 345°C, to minimize the energy consumption of LPG.

The deviations on the physico-chemical properties (density, viscosity, and refractive index) of distillation fractions compared to physico-chemical properties of pure MMA, indicating that high purity MMA was obtained after distillation.

The cumulative mass of reaction liquid products shows a first order kinetic behavior, with a root mean square (r^2) deviation of 0.99, showing a maximum between 90-100 minutes. The cumulative yield of reaction liquid products increases exponentially, with a root mean square (r^2) deviation of 0.98, showing a maximum between 90-100 minutes, remaining almost constant between 100 and 130 minutes. In addition, the MMA concentration between 80 and 110 minutes, decreases drastically from 97.76% to 88.00% (wt.), showing that reaction time should not exceed 80-90 minutes.

By thermal degradation of cross-linked PMMA-based dental resins scraps at 345°C and 405°C, one observes that high concentrations of MMA are achieved around 30 minutes, decreasing with reaction time up to 80 minutes, whereas a drastic decrease occurs between 80 and 130 minutes, corroborating to assert that reaction time should not exceed 80-90 minutes.

The concentration profile of methyl iso-butyrate, a side reaction product, by pyrolysis of cross-linked PMMA-based dental resins scraps at 345°C, 1.0 atmosphere, 30, 40, 50, 60, 70, 80, and 110 minutes, increases with reaction time in a sigmoid fashion, reaching around 3.75% (area.) at 110 minutes. In addition, the concentration profile of methyl iso-butyrate by pyrolysis of cross-linked PMMA-based dental resins scraps at 345, 405, and 420°C, 1.0 atmosphere, and 50 minutes, increases linearly with increasing temperature, being according to the results reported by Kaminsky and Frank [7].

SEM images of cross-linked PMMA-based dental resins scraps after pyrolysis shows that a drastic change, caused by complete carbonization of polymeric material, on the polymer morphology occurred.

Finally, the pyrolysis of cross-linked PMMA-based dental resins scraps makes it possible to depolymerize PMMA to recover large amounts of pure MMA.

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