THERMO-CATALYTIC PYROLYSIS OF UNRECYCLED PLASTIC WASTE IN A LAB-SCALE EXPERIMENTAL SET-UP: DETERMINATION OF OPTIMAL OPERATING CONDITIONS

A Thesis Submitted to
the Graduate School of Engineering and Sciences of
İzmir Institute of Technology
in Partial Fulfillment of the Requirements for the Degree of

MASTER OF SCIENCE

in Energy Engineering

by
Ecrin EKİCİ

December 2022
İZMİR

To my significant other, Umut, and our cats Şeker and Ayı

ACKNOWLEDGMENTS

I would like to thank Dr. Güray Yıldız as my advisor for all the opportunities in his research group and for challenging me during the process. I am also grateful that he is a role model for me on how to be a good researcher, academic, and teacher. Thanks to him, I am a more confident and open-minded researcher.

I would also thank my co-advisor, Dr. Başar Çağlar, for his support, academic advice, and non-stop positive energy. Also, I am very grateful to Dr. Magdalena Joka Yıldız for the internship opportunity in her laboratory, for sharing her valuable knowledge, and for showing other sides of renewable energy production.

I would like to thank my spouse for his non-stop support, care, and love. I could not finish this thesis successfully without him. Finally, I am grateful for having my cats during this journey with me.

ABSTRACT

THERMO-CATALYTIC PYROLYSIS OF UNRECYCLED PLASTIC WASTE IN A LAB-SCALE EXPERIMENTAL SET-UP: DETERMINATION OF OPTIMAL OPERATING CONDITIONS

370 million tons of polymers are produced worldwide annually (with an annual growth of 4%), of which *ca.* 16% are produced in the European Union (EU). By 2030, it is estimated that over 600 million tons of plastics will be produced. Plastic waste is a problem and will be severe day by day for the environment. This problem can easily switch to advantage by a carbon-neutral process: pyrolysis. This study analyzed and compared reported literature data with the experimental findings obtained in a continuously operated bench-scale pyrolysis reactor. The optimal conditions of the feedstocks' N_2 flow rate, feed intake, and mixing ratio for maximizing liquid production were estimated for pyrolysis by Taguchi's orthogonal array design. Optimized process parameters were used for the pyrolysis of fresh and waste counterparts of HDPE, LDPE, PP, and a defined mixture of those (25:25:50 wt.%) at 450°C. The tail gases of mixed fresh and waste POs were also examined for energy autonomy of pyrolysis. Fresh plastics yielded more liquid compared to waste plastics. Blending polyethylenes with PP improved the conversion efficiency and favored the formation of gasoline-range hydrocarbons while limiting the wax formation. The total energy potential of produced NCGs, mainly composed of C3 hydrocarbons, was found to be sufficient; the energy demand for endothermic bond breaking during pyrolysis was met in a range of 139 to 464% for various plastic types tested.

ÖZET

GERİ DÖNÜŞTÜRÜLMEMİŞ PLASTİK ATIKLARIN LABORATUVAR ÖLÇEKLİ BİR DENEY DÜZENEĞİNDE TERMO-KATALİTİK PİROLİZİ: OPTİMAL ÇALIŞMA KOŞULLARININ BELİRLENMESİ

Dünya çapında yılda, %16'sı Avrupa Birliği'nde (AB) olmak üzere, 370 milyon (yıllık %4'lük bir büyüme ile), ton polimer üretilmektedir. 2030 yılına kadar 600 milyon tonun üzerinde plastik üretileceği tahmin edilmektedir. Plastik atık, çevre için her geçen gün ciddileşen bir sorundur. Bu problem, karbon nötr bir süreçle kolaylıkla bir avantaja dönüşebilir: Piroliz. Bu çalışmada, rapor edilen literatür verileri analiz edilmiş ve sürekli çalışan laboratuvar ölçekli bir piroliz reaktöründe elde edilen deneysel bulgularla karşılaştırılmıştır. Sıvı üretim verimini artırmak için N_2 akış hızı, besleme hızı ve beslemenin karışım oranının optimal koşulları, Taguchi'nin ortogonal dizi tasarımı ile piroliz için tahmin edildi. İşlenmemiş ve atık yüksek ağırlıklı polietilen (HDPE), alçak ağırlıklı polietilen (LDPE) ve polipropilenin (PP) tek olarak ve polefinlerin (PO) karışımlarının (ağırlıkça %25:25:50) 450°C'de pirolizi için optimize edilmiş proses parametreleri kullanıldı. İşlenmemiş ve atık karışım PO'ların yan ürünü olan kalıcı gazların da pirolizin enerji özerkliği için incelenmiştir. İşlenmemiş plastiklerden, atık plastiklere kıyasla daha fazla sıvı üretidiği gözlemlendi. Polietilenlerin PP ile karıştırılması, dönüşüm verimliliğini iyileştirdi ve mumsu (yarı sıvı malzemeler) malzemelerin oluşumunu sınırlarken, benzin aralığında hidrokarbonların (C_5-C_{12}) oluşumunu destekledi. Ağırlıklı olarak C_3 hidrokarbonlardan oluşan üretilen kalıcı gazların toplam enerji potansiyeli yeterli bulundu; piroliz sırasında endotermik bağ kırılması için enerji talebi, test edilen çeşitli plastik türleri için %139 ila %464 aralığında karşılanmıştır.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

Plastics are inexpensive, durable, and adaptable materials that are primarily used in every area of our daily life to meet the needs of society. Polyolefins (HDPE, LDPE, PP), PS, PVC, PET, and other plastics (*e.g.,* ABS, PMMA) are the common plastic types that are mostly utilized in packaging, building, construction, textile, and automotive industries (Jubinville et al. 2020). The demand and production of plastic are growing simultaneously. Plastic production, excluding recycled plastics,, increased from 335 Mt to 367 Mt (*ca.* +9.6 %) for the last 5 years, between 2016 and 2020, around the world (PlasticEurope 2021). The production of virgin plastic decreased by 8.3% for EU27+3 thanks to the plastic waste management regulations of the European Commission, which are following the "Waste to Energy" (WtE) approach (Armenise et al. 2021; PlasticEurope 2021).

Renewable and sustainable waste management methods are gaining popularity to help decrease carbon emissions and slow down climate change. Properly separated and cleaned plastics can be re-extruded and re-shaped several times by mechanical recycling until the quality of the recycled plastic is not enough for the market (Panda, Singh, and Mishra 2010). Plastics with low quality for remolding are suitable feedstock for fuel production via thermochemical recycling methods. Pyrolysis is one of the thermochemical conversion methods applied to plastic for resource recovery in the absence of oxygen which leads to fuel-like products and valuable chemicals. Thanks to an oxygen-free environment during the process, none, or limited amounts of carbon dioxide (CO_2) and carbon monoxide (CO) are placed in the products depending on the plastic type and condition. As an example, pyrolysis of PET and waste polyolefins result in products with CO_x due to atomic oxygen in its molecular structure and oxygen-containing impurities, respectively (Maite Artetxe et al. 2010; Norbert Miskolczi, Bartha, and Angyal 2006). Energy recovery from plastics by incineration is another option in the scope of WtE, which has almost 50% more negative effects on climate change than pyrolysis (Jeswani et al. 2021). On the other hand, mechanical recycling of plastics has less carbon footprint compared to pyrolysis, but the direct comparison of life cycle

assessments of mechanical and pyrolysis is unnecessary since the feedstock relation is mentioned above (Davidson, Furlong, and McManus 2021). Besides the environmental benefits of the pyrolysis of plastics, studies focusing on the feasibility of the process prove its economic reliability (Fivga and Dimitriou 2018; Pacheco-López et al. 2021).

Oil is the targeted product in plastic pyrolysis, while gases and chars are the by-products that can be utilized as energy sources for a plastic pyrolysis process (Miandad et al. 2016). The content of plastic pyrolysis oil (PPO) varies with the operation mode (*i.e.*, thermal or catalytic) and type of plastic. For instance, during non-catalytic pyrolysis, the main product HDPE is a dark-colored liquid with high viscosity (*i.e.*, wax), while waxes were degraded to gasoline and diesel range hydrocarbons (*i.e.*, light oils) in the presence of a catalyst (Zeaiter 2014; N. Miskolczi et al. 2009). The light oils show similarities with petroleum-derived fuels in terms of physicochemical properties such as calorific value (Salaudeen et al. 2021), percentage of aromatic hydrocarbons (Elordi et al. 2011), and viscosity (Miandad et al. 2016). Several studies showed that plastic-derived fuel could be dropped into fuel to be utilized in compression-ignition (CI) and internal combustion (IC) engines without any upgrading (Devaraj, Robinson, and Ganapathi 2015; Singh, Ruj, Sadhukhan, Gupta, et al. 2020; Sunaryo et al. 2019). Utilization of the light oils in a CI or IC engine releases an insignificant amount of sulfur dioxide (SO_2) and nitric oxide (NO_x) (Elordi et al. 2011), but it increases the amount of CO_2 compared to commercial diesel (Mani, Subash, and Nagarajan 2009). On the other hand, waxes need to be further cracked before utilization in the engines as a fuel. Waxes are evaluated in lubrication, cosmetic, and coating materials as they can be an alternative energy source for pyrolysis (Sultan Majed Al-Salem and Dutta 2021).

Non-catalytic pyrolysis offers a simple-to-operate and cheap solution for plastic recycling. More than 90 wt% of plastics fed to a reactor can be completely converted to products, according to many studies (Diaz-Silvarrey, McMahon, and Phan 2018; Neves et al. 2007; Lopez et al. 2010; Miriam Arabiourrutia et al. 2017). Optimum process parameters for pyrolysis need to be determined to maximize the yield. The most important process parameter affecting conversion efficiency and fuel quality is temperature (Miandad et al. 2016; Moorthy et al. 2020). Increasing vapor residence time also promotes further cracking and production of lighter hydrocarbons (Zhao et al. 2020; Berrueco et al. 2002). Both the temperature and vapor residence time are directly relevant to reactor design. Reactors should offer adequate heat and mass transportation to get maximum conversion efficiency and quality (Panda, Singh, and Mishra 2010). Due to their easy and

low-cost operations microreactors, thermogravimetric analyzers (TGA) and batch reactors such as fixed bed reactors are the most used reactors (Lopez et al. 2017). Gas chromatography-mass spectroscopy (GC-MS) coupled microreactors enable direct identification of products of pyrolysis sensitively (Li et al. 2003; Yildiz, Ronsse, and Prins 2017), while TGA gives information about the reaction kinetics of thermal pyrolysis (Aboulkas, El, and Bouadili 2010). Although no specific feeding unit design and particle size are needed for batch reactors, removal of residues from a reactor, remaining corrosive products in a reactor, blockage in equipment by waxes, and low heat transfer rates are their main problems (Scheirs 2006). These reactors cannot mimic industrial pyrolysis processes because of scale-up difficulties (Yildiz, Ronsse, and Prins 2017). To be in line with real processes, continuously operated reactors are studied by many researchers. Fluidized bed reactors (Park, Jeong, and Kim 2019; Jung et al. 2010), continuously spotted bed reactors (Elordi et al. 2011; Miriam Arabiourrutia et al. 2017; M. Arabiourrutia et al. 2012), continuously stirred reactors (Frączak, Fabiś, and Orlińska 2021; Zayoud et al. 2022), screw kiln reactors (Sultan Majed Al-Salem et al. 2020; Zeller et al. 2021) and continuously operated tube reactors (Borsodi et al. 2011; Fekhar, Zsinka, and Miskolczi 2019) are preferred for pyrolysis of plastics by researchers to avoid heat and mass transfer limitations and easy control of temperature and residence time that maximize quality and quantity of products.

In this review, we focused on research articles published between 1984 and 2021 that concern non-catalytic and continuously operated pyrolysis for a single type, mixture, waste, or virgin plastics. Also, we developed a critical approach to the best conditions for operating parameters and units for the production of PPO.

1.1. The Influence of Plastic Type on the Pyrolysis Process

The feedstock types (plastics for this case) are the most important process parameters that affect product quality and quantity. Understanding the physicochemical properties of plastics (*e.g.,* volatile content, carbon, hydrogen, and oxygen content) by ultimate and proximate analysis is important to decide the suitability of plastics for pyrolysis to produce oil. As an example, oxygen and heteroatoms are not wanted elements for the sake of oil quality while a high volatile matter is an advantage for oil production. Also, performing the thermal analysis (*i.e.,* thermal gravimetric analysis (TGA) and

differential scanning calorimetry (DSC)) helps to define a temperature range for pyrolysis.

The condition of plastics is also important for the yield and quality of products. The product distribution of virgin and pure plastics is different because of contaminants inside waste plastics. As an example, char production is uncommon for fast pyrolysis of pure PEs (Frączak, Fabiś, and Orlińska 2021) while contaminants (*e.g.,* inorganic species) in waste plastics enhance the yield of solid products (Jung et al. 2010). On the other hand, the chemical structures of a repeating unit of plastics affect an aliphatic-to-aromatic ratio in liquid products. Linear chain plastics (*e.g.,* POs) produce more aliphatic hydrocarbons by non-catalytic pyrolysis (Berrueco et al. 2002; Jin et al. 2018; Predel and Kaminsky 2000) in contrast to plastics having an aromatic ring in repeating units (*e.g.,* PS) which leads to aromatic hydrocarbon majority pyrolysis oil (Maite Artetxe et al. 2015; Park et al. 2020; Zayoud et al. 2022).

1.1.1. Polyolefins

The most studied plastics in continuously operated pyrolysis are polyolefins (POs) (*i.e.,* HDPE, LDPE, and PP) since their physicochemical properties are suitable for pyrolysis conditions besides their dominant abundance in plastic waste streams. In Figure 1.1 (PlasticEurope 2021), the distribution of plastic types and their utilization areas are shown These plastics have suitable physicochemical properties such as high volatile matter (> 99 wt.%) and trace ash content in addition to high carbon to hydrogen ratio (*ca.* 6.6) which indicates a high calorific value (Phyllis2 2022). Incineration of 10 wt.% of fed POs for pyrolysis meets the energy requirements of endothermic bond cracking of 100 kg POs (Dispons 2006). Although the incineration of plastics enhances CO_2 emissions (Vollmer et al. 2020), it could be a good solution for both the volume reduction of plastics (Goodship 2007) and an energetically self-sustained pyrolysis process.

Non-catalytic pyrolysis of POs generally leads to wax-like products ($> C_{21}$ hydrocarbons) due to their long linear chains (Elordi et al. 2011; J. Aguado et al. 2002; Miriam Arabiourrutia et al. 2017). At a temperature higher than 600 ℃, gas production is generally enhanced due to secondary reactions (see 4.1.) (Yang et al. 2022). However, below the temperature, it is generally not sufficient to crack long chains of POs to

4

produce lighter hydrocarbons by pyrolysis (Elordi et al. 2011). For instance, R. Aguado et al. (2002) reported that the oil product obtained in a continuously spouted bed reactor (CSBR) is completely composed of C_{21+} hydrocarbons for temperatures 450 ℃, 500 ℃, 550 ℃, and 600 ℃. On the other hand, using a catalyst decreases the temperature of pyrolysis of POs (Anuar Sharuddin et al. 2016) and heavy hydrocarbon production in addition to improving the quality of pyrolysis oil by selectivity PS

Polystyrene (PS) which is produced from styrene monomer is used often as food boxes and packaging material. PS with high volatile content (*ca.* 99.5 wt.%) is suitable for pyrolysis (Sultan M. Al-Salem 2018). Many studies reports that the liquid product of pyrolysis of PS is majorly composed of styrene and styrene derivative chemicals (Dement'ev et al. 2019; Frączak, Fabiś, and Orlińska 2021; Maite Artetxe et al. 2015). Aromatic compounds such as benzene and toluene are secondary compounds in liquid products. Increasing temperature of pyrolysis inhibits styrene production, while BTX formation is accelerated (Maite Artetxe et al. 2015; Peng et al. 2022). Although, the composition of the liquid product of pyrolysis of PS indicates that the liquid product is desirable and valuable, traditionally and thermally pyrolyzed PS's liquid is thermal-oxidatively unstable due to amount of double bonds chemicals in the liquid (Park et al. 2020). Using a catalyst (Mertinkat et al. 1999) and a pretreatment reactor (*e.g.,* auger reactor) (Park et al. 2020) can both enhance the oil stability and adjust the yield of the aromatic content in oil according to the requirements set by the authorities. Another approach for valorization of PS is mixing it with POs as feedstock for pyrolysis to increase both liquid yield and aromatic content in a liquid (Frączak, Fabiś, and Orlińska 2021).
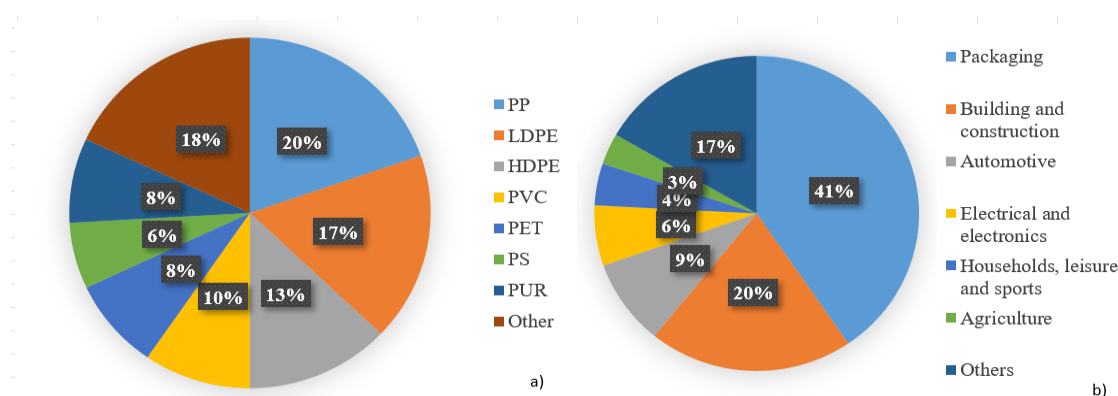
Figure 1.1. a) Plastic type distribution and b) utilization areas of plastics.

1.1.2. PS

Polystyrene (PS) which is produced from styrene monomer is used often as food boxes and packaging material. PS with high volatile content (ca. 99.5 wt.%) is suitable for pyrolysis (Al-Salem, 2018). Many studies reports that the liquid product of pyrolysis of PS is majorly composed of styrene and styrene derivative chemicals (Artetxe et al., 2015; Dement'ev et al., 2019; Frączak et al., 2021). Aromatic compounds such as benzene and toluene are secondary compounds in liquid products. Increasing temperature of pyrolysis inhibits styrene production, while BTX formation is accelerated (Artetxe et al., 2015; Peng et al., 2022). Although, the composition of the liquid product of pyrolysis of PS indicates that the liquid product is desirable and valuable, traditionally and thermally pyrolyzed PS's liquid is thermal-oxidatively unstable due to amount of double bonds chemicals in the liquid (Park et al., 2020). Using a catalyst (Mertinkat et al., 1999) and a pretreatment reactor (e.g., auger reactor)(Park et al., 2020) can both enhance the oil stability and adjust the yield of the aromatic content in oil according to the requirements set by the authorities. Another approach for valorization of PS is mixing it with POs as feedstock for pyrolysis to increase both liquid yield and aromatic content in a liquid (Frączak et al., 2021).

1.1.3. PET and PVC

PET has lower volatile content (*i.e.,* 86.75-91.75) compared to POs and significantly high amount of oxygen (*ca.* 32.9 wt.%) (Phyllis2 2022; Jahirul et al. 2022). Pyrolysis of PET produce low amount of liquid that is composed of mainly oxygenated hydrocarbons (*e.g.,* aldehydes and ketones) (Yoshioka et al. 2004; Maite Artetxe et al. 2010). The oxygenated hydrocarbons are unwanted in oils since they spoil the quality of oils by decreasing the calorific value and stability of oils (Bridgwater 1996). On the other hand, high amount of char which is majorly composed of terephthalic acid and benzoic acid and CO and CO_2 rich gas are formed by pyrolysis of PET because of oxygen content (Peng et al. 2022). The studies reports that the yield of oxygen containing hydrocarbons decreased in liquid products with increasing temperature (Maite Artetxe et al. 2010; Yoshioka et al. 2004). However, an increase in pyrolysis temperature diminishes the yield

of liquid product while the yields of gas and solid products enhanced. All in all, PET is not a suitable plastic type for high quality oil production by pyrolysis.

PVC is another plastic type which is not suitable for pyrolysis due to high amount of chlorine content (*i.e.,* 48-57 wt.%) (Jahirul et al. 2022) and considerably low volatile matter (*ca.* 91 wt.%) (Phyllis2 2022). During pyrolysis of PVC, chlorine content is converted to HCl gases which is highly hazardous for the environment and process equipment. Another drawback is that low amount of liquid is produced by pyrolysis of PVC since its most of the volatile content is chlorine (*e.g.,* 56 wt.%) (Kaminsky 1991; Scott et al. 1990). Also, liquid with chlorinated hydrocarbons which is produced by conventional pyrolysis is unwanted for the benefit of quality of liquid and the equipment. To overcome the drawbacks, some studies reported that using a two stage non-catalytic pyrolysis instead of a single stage non-catalytic pyrolysis removes most of the chlorine gases in the form of HCl. Two stage pyrolysis contains two reactors (Park et al. 2019, 2018): 1) A reactor being operated at temperature around 300 ℃ coupled with filter containing basic compounds such as CaO where HCl is captured; 2) A main reactor where pyrolysis occurs. Using a catalyst also helps to decrease Cl content in pyrolysis liquid (Peng et al. 2022).

1.2. Key Process Parameters

Optimization of process parameters such as temperature, vapor residence time and process duration play a crucial role in achieving the maximum yield of the targeted product and improving its quality. The adjustment and control of process parameters to achieve optimal conditions cannot be done in isolation from the reactor design. A reactor should ensure good heat and mass transfer during pyrolysis to overcome the high viscosity and low thermal conductivity of plastics. Therefore, continuously operated reactors (*e.g.,* continuously operated spouted bed reactors, continuously stirred tank reactors) are the focus of this study, as well as the possibility of scaling up continuous reactors to resemble industrial processes.

1.2.1. Temperature

Plastics are composed of a long chain of C-C and C-H bonds. Bond breakage energy of these bons require external energy to produce smaller chains so pyrolysis of plastics is an endothermic reaction (Yang et al. 2022). That is why temperature is a process parameter that significantly affects product distribution and quality. Pyrolysis of plastics are operated at a temperature range between 350 ℃ and 850 ℃ depending on the desired product (*i.e.,* oil, gas or char) (Kunwar, Cheng, et al. 2016). The optimum temperature of pyrolysis for producing maximum amount of liquid varies depending on plastic type, condition of plastic (*i.e.,* waste or virgin), and composition of mixtures. The composition of liquid products is also highly dependent on temperature. At temperatures between 350 ℃ and 500 ℃, non-catalytic pyrolysis of plastics mainly yields heavy products (*i.e.,* C_{21+} hydrocarbons) (M. Arabiourrutia et al. 2012; José F. Mastral, Berrueco, and Ceamanos 2006) due to brakeage of C-C bonds (Miandad et al. 2016) while increasing temperature up to 600 ℃, especially for POs, causes lighter liquid products like gasoline and diesel range hydrocarbons (*i.e.,* C_5-C_{12}) (Borsella et al. 2018; Zayoud et al. 2022). Elevating temperature higher than 600 ℃ is resulted with secondary cracking reactions that favors gas production (Yang et al. 2022).

1.2.2. Heating Rate

Heating rate is another process parameter that affects both the decomposition mechanism of plastics and the main product of pyrolysis. In general, slow pyrolysis is operated at lower heating rates (e.g., 10℃/min), which favors the production of solids, the maximum decomposition temperature is lower, while at fast heating rates such as 20000 ℃/min, the formation of liquids occurs (Papari, Bamdad, and Berruti 2021). The results of thermogravimetric analysis show that the change of heating rates has no significant effect on mass loss (Xu et al. 2018; Saad et al. 2021; Diaz Silvarrey and Phan 2016). In contrast, a wider decomposition temperature range and an increase in maximum degradation temperature occur when the heating rate is increased (Xu et al. 2018).

1.2.3. Carrier Gas and Vapor Residence Time

Pyrolysis is maintained in an inert environment provided by a carrier gas or fluidizing gas such as nitrogen (most commonly used), helium, and argon. In some studies, non-condensable gasses generated during pyrolysis can be used as carrier gasses (Park et al. 2020; Jung, Kim, and Kim 2013; Kang, Kim, and Kim 2008; Predel and Kaminsky 2000; Kaminsky 1991). Non-condensable gasses as fluidizing gases contain H_2 and C_1-C_4 hydrocarbons, which increase the formation of benzene-toluene-xylene (BTX) and polyaromatic hydrocarbons (PAH) by hydrogen abstraction from radical cyclic compounds (*e.g.,* phenyl groups) (Park et al. 2020; Lopez et al. 2017). In addition, inert gases sweep the hot vapors out of the reactor, so the flow rate of an inert gas is directly related to the residence time of the vapors. The high flow rate means short vapor residence time and vice versa for the low flow rate.

Vapor residence time is the time until the hot vapors leave the reactor after formation by pyrolysis. In general, minimizing vapor residence time prevents secondary cracking reactions and maximizes liquid yield (Peng et al. 2022). However, the vapor residence time should be regulated according to the operating temperature and type of plastic used as a feedstock. Examples of change in liquid composition varying with residence time and plastic types are given in Table 1.1. Increasing the vapor residence time slightly at moderately low temperature (~450 °C) leads to the production of lighter liquid products without significantly affecting the overall liquid yield by thermally cracking waxes to lighter product (Liu, Qian, and Wang 2000; Serrano et al. 2001). In contrast, instant removal of hot vapors at high temperatures (T $\geq$ 600 °C) eliminates excessive cracking (Miriam Arabiourrutia et al. 2017; Elordi et al. 2011). However, an operating reactor at high temperatures increases the cost of the process so maintaining non-catalytic pyrolysis at moderate temperature with elevated vapor residence time is a more cost-efficient way.

1.2.4. Thermal Pretreatment Applications

Feeding plastics to a pyrolysis reactor can be challenging for continuous operating systems. Feeding units generally are hoppers that require a specific particle size. Since

plastics are highly viscosity and low thermal conductivity, feeding plastics whose temperature below its melting temperature suppress mass and heat transfer in a reactor. Using a thermal pretreatment reactor such as melter tank and extruder reduces the time required to reach the pyrolysis temperature that limits the yields of by-products (*e.g.,* char) activated by slow pyrolysis (Papari, Bamdad, and Berruti 2021). Melt plastics are more non-viscous in nature than its solid form that eases the transferring it into the main reactor where pyrolysis takes place.

Pretreatment reactors provide some advantages concerning mass and heat transfer limitations that directly affect the product yields and quality. Also, contaminants and unwanted species like Cl, Br in feedstocks, especially waste plastics, are separated in the pretreatment reactors so the products formed in the main reactor have better quality (Park et al. 2018). However, it should be kept in mind that adding a pretreatment reactor into a system causes additional capital and maintenance cost. For noncatalytic pyrolysis of plastics, fuels whose physicochemical properties are sufficient for utilizing in an internal combustion engine cannot be achieved even in a well-optimized system. That is why using a pretreatment reactor at considerably mild conditions helps to eliminate mass and heat transfer struggles. Thus, using a pretreatment reactor helps to produce fuels that covers more restrictions such as viscosity and tortuosity for fuels set by local authorities. As an example, more gasoline-like hydrocarbons were produced from noncatalytic pyrolysis of PS by Park et al. (2020) compared to Williams & Williams (1997)'s study, although vapor residence time is fifteen times higher for Williams & Williams (1997)'s experiments. The main difference is between two is melt PS at 200 °C by an extruder was used as a feedstock for Park et al. (2020)'s work.

1.3. Reactor Types

Improving liquid yield and quality by optimizing process parameters cannot be accomplished without a separate consideration of reactor type. Batch and/or semi-batch reactors which are generally utilized on a laboratory scale, allow easier operations, but their non-flexible structure restricts controlling and tailoring the operational parameters. On the other hand, continuously operated reactors, and are hence, prone to be scaled and used in large-scale industrial processes. This study focuses only on continuously operated

reactor types. In Figure 1.2, the statistical information of reactor types used for continuous and non-catalytic pyrolysis of plastics is shown.

1.3.1. Fluidized Bed Reactors

Fluidized-bed reactors (FBRs) which are shown in Figure 1.3 (Zhao et al. 2020), are the most preferred reactor type for continuous and thermal pyrolysis. FBRs are filled with neutral particles (*e.g.,* sand, silica) fluidized with a fluidizing agent (gas) (*e.g.,* N_2, product gas). Since the medium in the reactor acts as a heat transfer medium carrier and the fluidized particles allow good mixing, FBRs overcome the limitations of heat and mass transfer. Apart from these advantages, a short vapor residence time can be achieved in FBRs, which is both practical for maximizing liquid production and forming uniform product spectrum from plastics by pyrolysis (Jung et al. 2010; Cho, Jung, and Kim 2010). Temperature and vapor residence time, the key process parameters that directly affect product yield and composition, should be carefully selected to maximize the quality and quantity of the target product. The studies show that the operation of FBRs at a temperature higher than 600 ℃ for the pyrolysis of POs favors gas products even if the vapor residence time is less than one second (Berrueco et al. 2002; Park et al. 2019; Park, Jeong, and Kim 2019). In contrast, pyrolysis of POs at lower temperatures (*e.g.,* 500 ℃) and a vapor residence time of more than 10 seconds produces a liquid of 72.7 wt. % (Zhao et al. 2020). On the other hand, melt plastics sticks on the neutral solids in FBRs that lead segregation and fluidization problem (M. Arabiourrutia et al. 2012; Yildiz, Ronsse, and Prins 2017).

1.3.2. Continuously Spouted Bed Reactors

Continuously spouted bed reactors (CSBRs) are more complex in design compared to FBRs but provide more efficient heat and mass transfer during pyrolysis and can also handle a wider range in particle sizes. CSBRs also use solid particles in a bed to fluidize. Pyrolysis of plastics occurs in two steps in CSBRs: 1) covering of sand particles with molten plastic; 2) cyclic movement of particles during pyrolysis (see Figure 1.4 (Maite Artetxe et al. 2015)) (Miriam Arabiourrutia et al. 2017). These steps eliminates

segregation and fluidization drawback which is common for FBRs (Elordi et al. 2011). CSBRs enable flash pyrolysis conditions, allowing complete conversion of plastics to a liquid product (M. Arabiourrutia et al. 2012; Elordi et al. 2011; Lopez et al. 2010).

1.3.3. Continuous Flow Stirred Tank Reactors

Continuous flow stirred reactors (CSTRs) are another suitable reactor type for pyrolysis of plastics. Stirring mechanism of CSTRs offer uniform heat distribution while decreasing amount of residues on the wall of reactors that behaves like an insulator (Gebre, Sendeku, and Bahri 2021; Kartik et al. 2022). Using an extruder as a thermal pretreatment reactor before feeding a plastic to the main reactor is generally applied in lab-scale studies (Frączak, Fabiś, and Orlińska 2021; Auxilio et al. 2017; Murata, Brebu, and Sakata 2010; Lei et al. 2018; Murata et al. 2002; Murata, Brebu, and Sakata 2009b; Zayoud et al. 2022; Miller, Shah, and Huffman 2005) and in some industrial applications (*e.g.,* THERMOFUEL process, SMUDA process) (Kartik et al. 2022). Melt feedstocks help to avoid distributing thermal uniformity. Thanks to these advantages, more than 90 wt.% of liquid containing mostly lightweight hydrocarbons (*i.e.,* C_5-C_{20}) at considerably low temperatures (< 450 ℃) (Murata et al. 2002; Murata, Brebu, and Sakata 2009a).
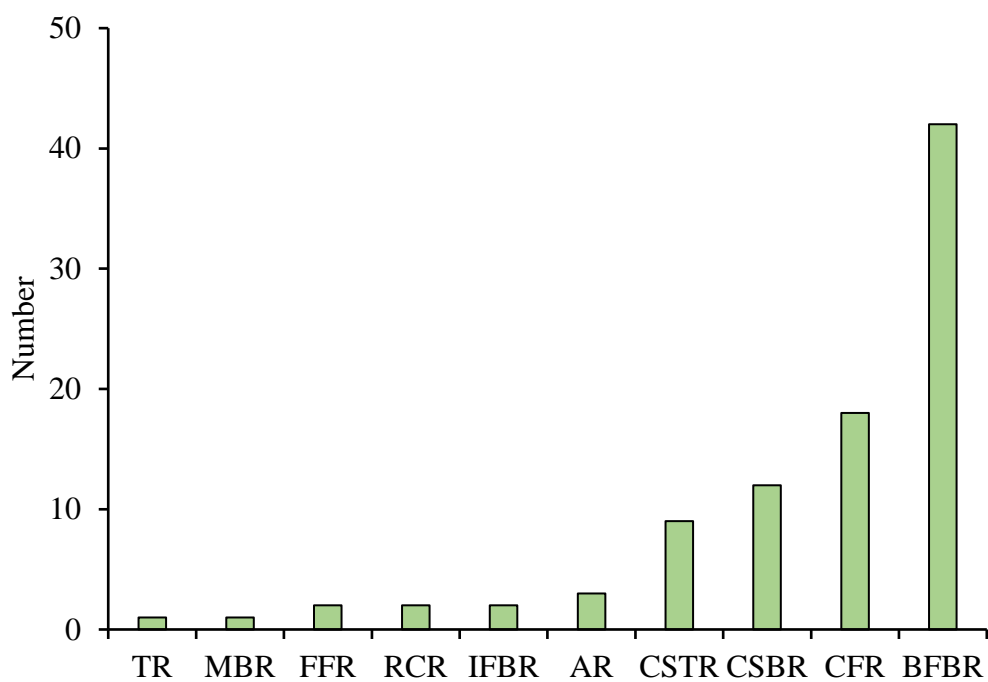
Figure 1.2. Statistical information of reactor types used for non-catalytic and continuously operated pyrolysis.
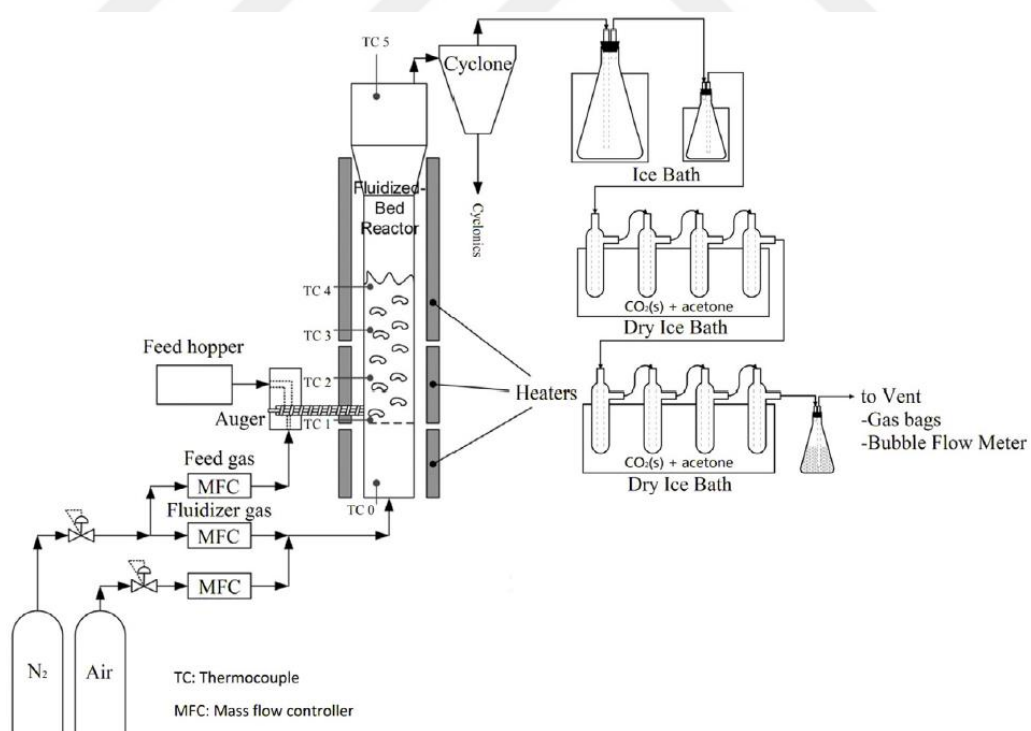
Figure 1.3. A schematic representation of an FBR.

Table 1.1. Liquid yield and compositions of plastics varying with pyrolysis temperature.

Plastic type	Temperature (°C)	Vapor residence time (s)	Liquid product yields (wt.%)				Ref.
			Gasoline range (C_5-C_{12})	Diesel range (C_{13}-C_{20})	Wax (C_{21+})	Total	
HDPE	450	0.02	0	0	80	80	[52]
HDPE	450	0.05	0.8	19.2	80	100	[35]
HDPE	500	1.58	5.83	21.2	70.3	97.4	[67]
HDPE	600	0.05	16.1	22.9	55.6	94.5	[24]
HDPE	700	0.01	32	16	12	60	[15]
LDPE	450	0.05	1.2	18.8	80	100	[35]
LDPE	450	15	25.4	31.6	42	99	[76]
LDPE	500	0.05	3.7	27.3	69	100	[35]
LDPE	500	13.4	28.1	14.3	38.8	81.2	[26]
LDPE	700	2.5	NaN	NaN	NaN	30.8	[77]
PP	450	0.02	0	0	92	92	[52]
PP	510	5.6	6.4	28.8	56.2	92.9	[43]
PP	600	0.05	3.8	46.2	50	100	[35]
PS	450	0.3	72.7	11	14	97.6	[75]
PS	420	16	57.7	14.5	7.6	79.8	[78]
PS	500	0.05	59.1	34.4	0	93.6	[44]
PS	515	3	99.7	0	0	99.7	[58]
PS	600	0.3	87.2	12	0	98.7	[75]

*TR: Thermal reactor; MBR: Moving bed reactor; FFR: Free fall reactor; IFBR; Internally circulating fluidized bed reactor; AR: Auger reactor; CSTR: Continuously stirred tank reactor; CSBR: Continuously spouted bed reactor; CFR: Continuous flow reactor; BFBR: Bubbling fluidized bed reactor.
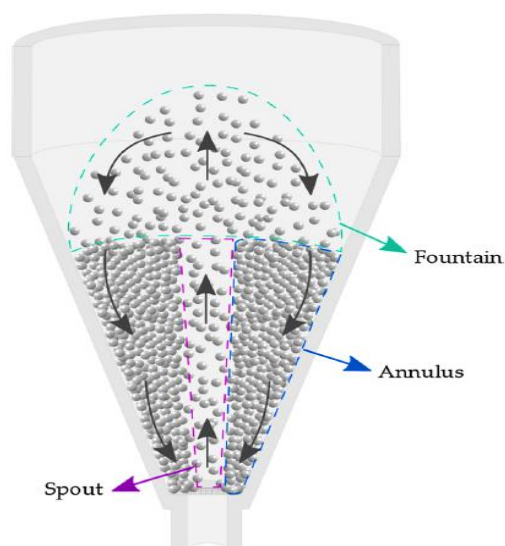
Figure 1.4. A schematic representation of a CSBR.

1.3.4. Other Types of Reactors

Continuous flow tube reactors (CFRs), auger reactors (ARs), and rotating cone reactors (RCRs) are the other types of continuous flow reactors that are used for pyrolysis of plastics in literature. These reactors are mainly designed to overcome mass and heat transfer limitations, but they have both advantages and disadvantages. CFRs have simple design and can be easily operated. CFRs are heated outside and contain no bed or heat carrier. The main drawback for CFRs is heat transfer limitations. Auger reactors, or screw reactors, are portable reactors that can be easily utilized where feedstock is available (Jahirul et al. 2022). ARs are not easily scaled-up and require proper attention in the design step. Also, soft feedstock such as plastic bags can get tangled during pyrolysis which is another drawback. Feedstocks and heated sand are fed to RCRs simultaneously that improves heat transfer. Feedstock and sand are rotated up while pyrolysis occurs. RCRs have several advantages such as simple solid separation, improved heat transfer and no need for carrier gas (Westerhout et al. 1998a, 1998b). RCRs can plugged and have poor mixing at radial direction (Dai et al. 2022).

1.4. Kinetic Behavior of Plastics in Pyrolysis

Performing thermal gravimetric analysis (TGA) to learn at which temperature pyrolysis starts and ends while differential gravimetry (DTG) shows the maximum temperature of mass loss. Both analyses are crucial before designing an experiment set to get maximum yield of a target product with high quality.

TGA results shows that lower heating rates such as 5 ℃/min leads more residual mass, while lower amount of solid product is observed for higher heating rates (Papari, Bamdad, and Berruti 2021). The trend proves that instant heating of reactors to the pyrolysis temperature leads to more volatile products, namely liquid and gas.

Thermal behavior of plastics shows different trend measure by TGA (see Table 1.2) based on their branches or linearity in physical form. As an example, maximum decomposition occurs at lower temperatures for PS and PET due to its branched property compared to linear polymerized plastics (*e.g.,* HDPE) (Diaz Silvarrey and Phan 2016). PVC also behaves differently under thermal composition. PVC shows two mass loss steps: 1) Chlorine removal step; 2) Pyrolysis step

Table 1.2. Thermal behavior of several plastics.

Plastic Type	Decomposition temperature range	Temperature of maximum mass loss	Heating rate (℃/min)	Ref.
PET	395-520	425	10	(Diaz Silvarrey and Phan 2016)
	369-579	430	10	(Saad et al. 2021)
HDPE	425-565	470	10	(Diaz Silvarrey and Phan 2016)
	397-500	480	10	(Saad et al. 2021)
PVC*	269-440; 440-592	342; 511	100	(Xu et al. 2018)
	283-336; 336-470		10	(Soudais et al. 2007)
LDPE	443-535	460	10	(Diaz Silvarrey and Phan 2016)
	359-500	460	10	(Saad et al. 2021)
	440-572	508	100	(Xu et al. 2018)
PP	415-540	450	10	(Diaz Silvarrey and Phan 2016)
	349-488	450	10	(Saad et al., 2021)
PS	349-488	450	10	(Saad et al. 2021)
	391-551	491	100	(Xu et al. 2018)
	372-452	400	10	(Diaz Silvarrey and Phan 2016)

*Two degradation steps available for PVC

CHAPTER 2

MATERIALS AND METHODS

2.1. Methodology for the Literature Survey

In this work, research articles published between 1984 and 2022, focusing on the pyrolysis of POs performed in continuously and non-catalytically operated process systems were investigated. The literature survey was conducted by using Web of Science, Scopus, and Wiley databases. The keywords used for the database search were designated as "high-density polyethylene", "low-density polyethylene", "polypropylene", "polyolefin"," polystyrene", "polyvinyl chloride", "polyethylene terephthalate" and "pyrolysis". Articles matching these keywords are collected and classified into two sets, *viz.* review articles and research articles. As a supportive step, the individual lists of references of the review articles were investigated further to expand the collected set of research articles. The data collection method is given in the flowchart in Figure 2.1.

In line with the industrial processes, a continuously operated pyrolysis process mode was focused, while non-catalytic (NC) pyrolysis was chosen to explain the trends in yields in the absence of any promoter (*i.e.,* catalysts, steam, reactive gases (*e.g.,* H_2)). A total of 96 research articles, fitting the abovementioned selection criteria, were collected and analyzed in terms of the reported product yields and energy values of the (by-)products. The data is further analyzed in terms of the process parameters, involving the plastic type, feed intake (g/min), reactor type, pyrolysis temperature (°C), vapor residence time (s), and product yields in the selected studies. The carrier gas flow rate and heating rate were not considered because these were only reported in a small number of the selected references. The mean values were included in the case of certain ranges reported.

2.1.1. The Methodology Used for Determination of Optimum Conditions for Maximum Gasoline Range Fuel Production from PP

14 articles, in total, concerning non-catalytic and continuous pyrolysis of PP were collected according to the data collection method mentioned above. The data concerning pyrolysis of PP was further analyzed in detail to explain optimum pyrolysis conditions for gasoline-like fuel production.

Thermal gravimetric analysis (TGA) shows that pyrolysis of PP occurs at temperatures between 415 ℃ and 540 ℃ under an inert gas (*e.g*., N_2) flow rate (Diaz Silvarrey and Phan 2016). The maximum cracking takes place for PP at 470 ℃ determined by differential thermal derivative thermogravimetry (DTG) (Saad et al. 2021). Also, many studies reported that almost a complete conversion of the initial mass of PP is measured by TGA (Xu et al. 2018; Diaz Silvarrey and Phan 2016). In the light of the kinetic data of PP, the maximum allowable temperature for pyrolysis was selected 550 ℃ (vertical dashed lines in Figure 1), while the lowest liquid yield was 70 wt.% (horizontal dashed lines in Figure 1) was selected considering possible experimental errors and the average yield data of the collected articles.

The data fulfilling the yield and temperature boundaries (upper-left section of Figure 1) were examined in terms of the detailed composition of liquid products varying with process parameters (*i.e.,* temperature and vapor residence time). The studies (Walendziewski 2005; Frączak, Fabiś, and Orlińska 2021; Jin et al. 2018) did not report any data about wax, gasoline, and diesel range hydrocarbons were excluded in this part even though the data was located between the temperature and the yield boundaries.

2.1.2. The Methodology Used for Determination of Optimum Conditions for Maximum Gasoline Range Fuel Production from HDPE

The data collection methodology was applied for this part. After the data was collected for non-catalytic and continuous pyrolysis of plastics, the data concerning pyrolysis of HDPE was separated. In total, 18 articles were collected that fall into the

category of *non-catalytic*; they were precisely examined and the reported information, such as the operational parameters (*i.e.,* temperature and residence time), process units (i.e., reactors), and product characteristics (*i.e.,* yields) were recorded in a Microsoft Excel file. The analysis was used to determine the optimum conditions for maximum production of C_5 to C_{12} hydrocarbons by thermal and continuous pyrolysis of HDPE.

Based on the reported results of TGA analyses, HDPE starts to crack at temperatures between 413 °C and 565 °C under a nitrogen atmosphere. The highest degradation rate was obtained at around 480 °C via DTG (Diaz Silvarrey and Phan 2016; Saad et al. 2021). Several studies report a 99 wt.% of conversion of the initial mass of HDPE in TGA (Kumagai et al. 2020). In light of these data, 600 °C and 70 wt.% were set as the highest allowable pyrolysis temperature and the minimum yield for pyrolysis oil production from HDPE (shown as dashed lines) Figure 3.2, respectively.

Gasoline range hydrocarbon production and wax cracking as a function of residence time were also investigated in CBRS and BFBRs (see Figure 3.3). Since no data were reported about the residence time of hot vapors in CSTRs in the non-catalytic set, CSTRs were omitted. For CSBRs, only the data falling into the pyrolysis oil production range were selected. Since all the reported data for BFBRs were out of the temperature limit, only the yield limitation mentioned above was applied to give a point of view for the vapor residence time. Based on the reported results, primary pyrolysis vapors were not allowed to stay longer than 0.27 and 1.5 seconds in CSBRs and BFBRs, respectively.

2.1.3. Analysis of Process Parameters and Assessing the Possibility of Utilizing the Tail Gases as Energy Sources for the Pyrolysis of Polyolefins

In this part, research articles published between 1984 and 2021, focusing on the pyrolysis of POs performed in continuously and non-catalytically operated process systems were investigated. The data collection method is given in the flowchart in Figure 3.4. In line with the industrial processes, a continuous pyrolysis setting was focused, while non-catalytic (NC) pyrolysis was chosen to explain trends in yields in the absence of any promoter (*i.e.,* catalysts). In total, 23 research articles were collected and deeply analyzed regarding the reported product yields and energy values of the (by-)products.
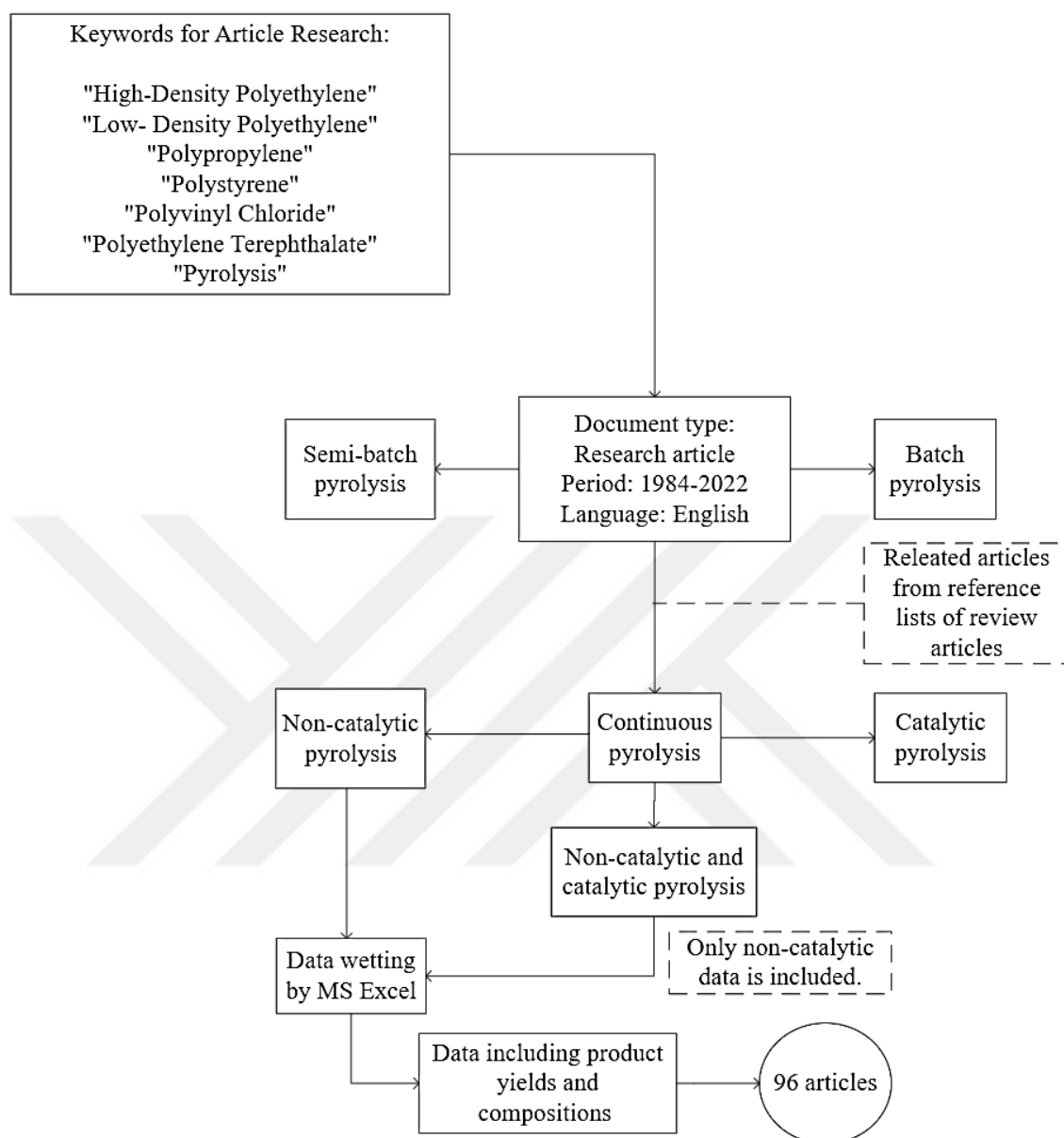
Figure 2.1. Methodology used for the data collection.

The highest degradation rates were obtained from differential thermogravimetry (DTG) at around 480 °C, 470 °C, and 460 °C for HDPE, LDPE, and PP, respectively (N. Miskolczi et al. 2009). On the other hand, the maximum decomposition temperatures vary between 470°C and 525°C depending on the composition of the mixture (Dubdub and Al-Yaari 2020; Chowlu, Reddy, and Ghoshal 2009; Singh, Ruj, Sadhukhan, and Gupta 2020). In general, LDPE causes a slower reaction and increases the activation energy of bond breaking while increasing the PP content of a POs blend lowers the pyrolysis

temperature Since PP has lower stability due to the third carbon in its monomer, resulting in lower bond breaking activation energy (Frączak, Fabiś, and Orlińska 2021; Dubdub and Al-Yaari 2020; Chowlu, Reddy, and Ghoshal 2009). In the light of the DTG data, the maximum allowable pyrolysis temperature was determined as 600 °C (shown as vertical dashed lines in Figure 3.4. Also, more than 90 wt.% conversions of the initial mass of POs were reported in many studies (Salaudeen et al. 2021; Elordi et al. 2011) Considering the thermal conversion data, possible experimental errors, and the average yield in our database mentioned in Figure 3.4., 70 wt.% is set as the minimum liquid yield (shown as horizontal dashed lines in Figure 3.4). The data falling in the optimal zone for liquid production (upper-left section of the chart) were further examined to explain the energy potential of the gas products (*i.e.,* C_1 to C_4 hydrocarbons) as by-products. The total combustion energy of gases was calculated by Equation (2.1), where E_{gas} and CV are the total energy of gas products and the calorific value, respectively (Fivga and Dimitriou 2018).

$$E_{gas} = CV_{CH_4} * Yield_{CH_4} + CV_{C_2H_4} * Yield_{C_2H_4} + CV_{C_2H_6} * Yield_{C_2H_6} + CV_{C_3H_6} * Yield_{C_3H_6} + CV_{C_3H_8} * Yield_{C_3H_8} + CV_{C_4H_8} * Yield_{C_4H_8} + CV_{C_4H_{10}} * Yield_{C_2H_{10}} + CV_{H_2} * Yield_{H_2}$$
<div align="right">2.1</div>

$$\% \ coverage \ for \ energy \ need = \left(\frac{280000}{E_{gas}}\right) * 100$$
<div align="right">2.2</div>

2.2. Design of Experiments

2.2.1. Taguchi Experimental Array Design to Determine Optimum Conditions

The Taguchi method uses orthogonal arrays to minimize the number of experiments and provide an accurate prediction of optimal conditions. The Taguchi method shows orthogonal arrays denoted as $L_a(b^c)$, where a is the number of experiments

required, b is the number of control factors, and c is the number of control factors to be analyzed. The Taguchi method is useful for explaining detailed information about the effects of control factors on outputs (Chen et al. 2014). The technique describes signal (S) and noise (N) outputs. Outputs are represented as S, while undesired outputs are described as N. The method predicts the optimal conditions for a design based on the signal-to-noise (S/N) ratio. S/N ratios as quality attributes are classified into three categories: "Larger is better", "Nominal the best", and "Smaller is better" (Alavi-Borazjani, Tarelho, and Capela 2021). Since the concept of the study is to maximize liquid production, the equation to calculate the S/N ratio for "Larger is better" is as follows

$$S/N_{LB} = -10 log \left[\frac{1}{n} \sum_{i=1}^{n} \frac{1}{y_i^2}\right] \qquad 2.3$$

where n is the number of experiments, and y_i is the liquid yield obtained from the ith experiment.

In this study, Taguchi experimental array design whose steps are given in Figure 2.2 is used to determine optimum process conditions for maximum liquid production of pyrolysis of fresh PP, LDPE and mixture of HDPE, LDPE, and PP. Pyrolysis temperature and process duration are 450 ℃ and 60 minutes for pyrolysis of pure PP, LDPE, and the mixture. For PP and LDPE, four control factors which are N_2 flow rate (A), feeding period (B), plastic amount per feeding (C), and temperature of the condenser (D), and three levels are selected. The experimental array designs of four control factors and their three levels and experimental layout using L9 (3^4) orthogonal array for PP are represented in Table 1, and Table 2, respectively. Similarly, Table 2.1 - Table 2.2 and Table 2.3 - Table 2.4 are the Taguchi experimental array design and L9 (3^4) orthogonal array for LDPE, respectively.

The other Taguchi experimental design is performed for mixture of pure HDPE, LDPE, and PP to understand effect of, N_2 flow rate (control factor A), feed intake (control factor B) and mixing ratio of plastics (control factor C) on liquid yield. The temperature and process duration are kept constant as 450 ℃ and 60 minutes respectively. Feeding period is chosen as 15 minutes considering optimum feed interval for pyrolysis of pure PP and LDPE. The mixing ratio of pure POs is shown in Table 2.5. The related designs for the mixed plastics are shown in Table 2.6 and Table 2.7.

The next step after the design of experiments is conducting the experiments. All experiments are repeated twice. Average yields and standard deviations of all products (*i.e.*, liquid, solid, and gas) are calculated. Data is accepted if the standard deviation is less than 5%.

Minitab software is used to determine the optimal conditions to maximize liquid yield for each design. Average liquid yields and standard deviations of each run are inserted into the software. Since maximum liquid yield is the goal, the "larger the better" formula (see Equation (2.3)) is selected in the software for calculating the optimal conditions for each control factor by using S/N ratios of each run. Once the optimal levels of the control factors are determined, the confirmation experiment is performed. The software also calculates the theoretical maximum yield of liquid products. The comparison of theoretical and experimental results is performed to verify whether the optimum conditions for maximum liquid yield are valid or not. The order of importance of the control factors is calculated by using S/N ratios.

Table 2.1. Pyrolysis of pure PP control factors and their levels.

	Level 1	Level 2	Level 3
Factor A: N$_2$ flow rate (L/min)	0.8	0.9	1.0
Feeding period (min), B	10	15	20
Plastic amount per feeding (g), C	10	20	30
Temperature of the condenser (℃), D	0	-12.5	-25

Table 2.2. Experimental layout using an L9 (3^4) orthogonal array for pure PP.

Run	A	B	C	D
1	1	1	1	1
2	1	2	2	3
3	1	3	1	2
4	2	1	1	1
5	2	2	2	2
6	2	2	3	3
7	3	1	3	2
8	3	2	1	3
9	3	3	2	1
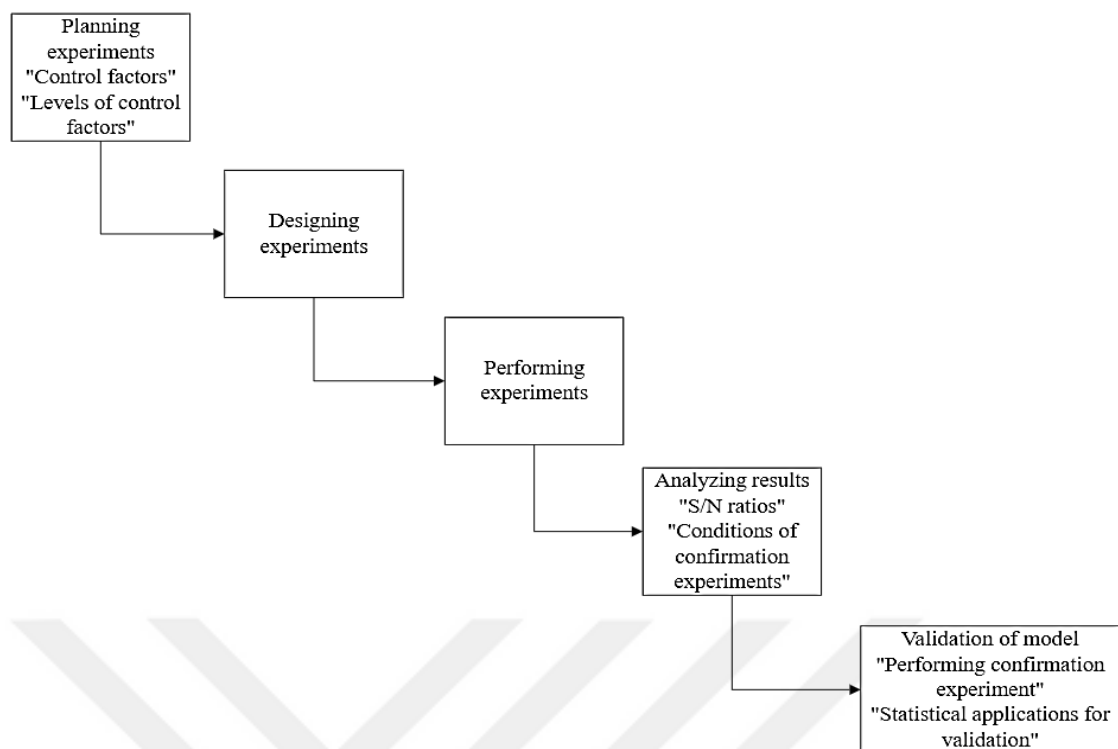
Figure 2.2. The steps of the design of experiment in this study.

Table 2.3. Pyrolysis of pure LDPE control factors and their levels.

	Level 1	Level 2	Level 3
Factor A: N_2 flow rate (L/min)	0.9	1.0	1.1
Feeding period (min), B	10	15	20
Plastic amount per feeding (g), C	10	20	30
Temperature of the condenser (℃), D	0	-5	-10

Table 2.4. Experimental layout using an L9 (3^4) orthogonal array for pure LDPE.

Run	A	B	C	D
1	1	1	1	1
2	1	2	2	2
3	1	3	3	3
4	2	1	2	3
5	2	2	3	1
6	2	3	1	2
7	3	1	3	2
8	3	2	1	3
9	3	3	2	1

Table 2.5. Mixing ratio of pure POs.

	HDPE (wt.%)	LDPE (wt.%)	PP (wt.%)
Mix 1	50	25	25
Mix 2	25	50	25
Mix 3	25	25	50

Table 2.6. Pyrolysis control factors and their levels for pure mixture of HDPE, LDPE and PP.

	Level 1	Level 2	Level 3
Factor A: N_2 flow rate (L/min)	0.9	1.0	1.1
Feed intake (g/min), B	1	1.5	3
Mix Type, C	Mix 1	Mix 2	Mix 3

Table 2.7. Experimental layout using an L9 orthogonal array for pure mixtures of POs.

Run	A	B	C
1	1	1	Mix 1
2	1	3	Mix 2
3	1	2	Mix 3
4	2	1	Mix 3
5	2	3	Mix 2
6	2	2	Mix 1
7	3	1	Mix 2
8	3	3	Mix 3
9	3	2	Mix 1

2.3. Experimental

2.3.1. Feedstock

In the pyrolysis experiments, fresh HDPE, LDPE, and PP granules (obtained from Petkim Petrokimya Holding A.Ş., Aliağa, İzmir, Türkiye), and their waste counterparts collected from the local residential plastic waste stream of Urla province of İzmir, were used as feedstocks. The physical properties of fresh plastics are shown in Table 2.6. Since a low melt flow index (MFI), which depends on the molecular weight of the polymers, means higher thermal stability, higher decomposition temperature, and higher viscosity

(Abbas-Abadi, Haghighi, and Yeganeh 2012), the MFI was chosen as high as possible. To facilitate mass and heat transfer during pyrolysis, the particle sizes of the plastics were chosen to be less than 4 mm because the thermal conductivity of the plastics is low (Dai et al. 2022). Waste plastics were categorized according to their resin code (ASTM International, n.d.) and separated and shredded to smaller sizes as shown in Figure 2.3.

The ultimate and proximate analyses of fresh and waste plastics as well as HHV, were shown in Table 4.1. The characteristics of waste plastics were determined experimentally, while the data were extracted from the database (Phyllis2 2022). As can be seen in the results, both fresh and waste plastics were composed of almost volatile content. C to H ratios (C/H) of waste plastics were similar to fresh POs but the oxygen content of waste plastics lessens HHVs.

Thermal behavior, TGA and DTG, results of the feedstocks used in this study were represented in Figure 4.1 a) and b), respectively. A detailed explanation of the thermal degradation of waste POs were listed in Table 4.2. The thermal decomposition temperature ranges of W-HDPE, W-LDPE, and W-PP were 458-501 ℃, 457-495 ℃, and 420-488 ℃ for 10 K/min heating rate, respectively. The maximum degradation occurs at temperatures 477.4 ℃, 472.5 ℃, and 456.3 ℃ for W-HDPE, W-LDPE, and W- PP, respectively. The peak temperatures are similar to the work of [22,72]. TGA and DTG curves of W-HDPE and W-LDPE show almost identical thermal behavior, while W-PP started to decompose significantly earlier and faster since PP having third carbon as its monomer has lower activation energy compared to LDPE and HDPE [36,95,96]. Another reason for the fast decomposition of WPP can be the number of recycling cycles [102]. The increase in several recycling cycles of POs changes their physical form 103]. The linearity of PP transforms to a liquid-like form by ageing, while PEs' linear chain becomes crosslinking [103].
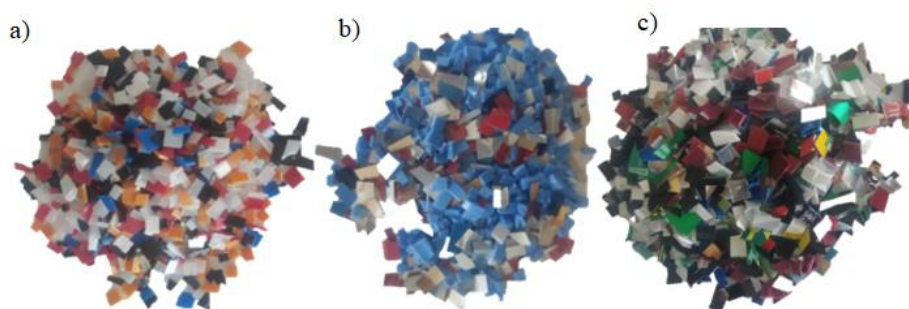
Figure 2.3. Shredded waste plastics a) HDPE, b) LDPE, and c) PP.

Table 2.8. Physical properties of pure plastics used in the experiments.

	Size (mm)	Melt flow index (g/10 min)	Density (g/cm3)	Melting point (°C)
LDPE	3.2	2.5	0.920	110
HDPE	3.6	5.5	0.965	134
PP	3.5	24	0.905	163

Table 2.9. The characteristics of fresh and waste feedstocks.

	Proximate analysis (wt.%)				Ultimate analysis (wt.%)					HHV (MJ/kg)
	Moisture	VM	Ash	FC*	C	H	O*	N	S	
F-HDPE[**]	0.0	100.0	0.0	0.0	85.6	14.4	0.0	0.0	0.0	44.6
F-LDPE[**]	0.0	100.0	0.0	0.0	85.6	14.4	0.0	0.0	0.0	44.6
F-PP[**]	0.0	100.0	0.0	0.0	85.6	14.4	0.0	0.0	0.0	47.3
F-Mix[**]	0.0	100.0	0.0	0.0	85.6	14.4	0.0	0.0	0.0	46.0
W-HDPE	0.3	97.1	1.0	1.6	85.1	14.4	0.5	0.0	0.0	45.4
W-LDPE	1.3	93.3	1.7	3.7	81.6	13.2	5.2	0.0	0.0	43.2
W-PP	0.4	94.8	2.3	2.6	80.9	13.5	5.6	0.0	0.0	43.0
W-Mix	0.6	95.0	1.8	2.6	82.1	13.7	4.2	0.0	0.0	43.7

*By difference

** HHV of fresh plastics are calculated by Milne equation. For FMix and WMix, the mixing ratio was used for calculation of HHVs.

*** The data was taken from (Phyllis2 2022).

Table 2.10. Thermal decomposition outcomes of waste POs from TGA and DTG.

Sample	TGA results			DTG results	
	Solid residue (wt.%)	Onset temperature (°C)	Weight loss (wt.%)	Peak temperature (°C)	Rate of degradation (%/min)
WHDPE	0.76	458.4	94.63	477.4	35.97
WLDPE	2.62	457.4	97.28	472.5	33.39
WPP	8.76	420.0	95.52	456.3	18.11

2.3.2. Experimental Procedure

Pyrolysis experiments were performed in a bench-scale setup of which a sketch is shown in Figure 3. The reactor vessel, 1 L in volume, was continuously purged with inert N_2 gas, of which the flow rate was fully controlled by a mass flow controller (Teledyne Hastings, HFC 302). The reactor was heated with 3.50 kW by a furnace (ISOLAB, Heating mantle). The time required for reaching from room temperature to the set temperature was 30 min. Continuous feeding of the feedstock was started subsequent to reaching the reaction temperature. The vapors were swept to the 2-necked round bottom flask where initial condensation of heavy hydrocarbons (*i.e.,* wax) took place. The diethylene glycol-water mixture was cooled down to -25 °C by a refrigerated cooler (CLS Scientific, CLRC 17R, power consumption 2.2 kW) and sent to a Liebig condenser where the rest of the pyrolysis vapors were condensed to form liquid products. The condensed lighter hydrocarbons were collected in the 2-necked round bottom flask. The flow rate of the non-condensable gases was screened through a gas meter (Federal, FN G4) measuring the volumetric flow rate in the range of 0.04 m^3/h and 6 m^3/h with an accuracy of 10^{-4} m^3/h. NCGs samples were collected in a Tedlar bag (GSB, 3L) and analyzed through a GC-TCD, accordingly.

The optimum conditions for pyrolysis of mixed plastics are 1.1 L/min N_2 flow rate, 1.5 g/min feed intake, and a mixing ratio of 25:25:50 (HDPE: LDPE: PP) by mass per cent. Based on these optimal conditions, two new sets of experiments were designed: Set-1 and Set-2 experiments. In Set-1, fresh HDPE (F-HDPE), LDPE (F-LDPE), and PP (F-PP), and waste HDPE (W-HDPE), LDPE (W-LDPE), and PP (W-PP) were pyrolyzed

at 450 °C under a constant N_2 flow rate of 1.1 L/min for 60 min process duration. Set-2 was designed to understand the effects of the catalyst on the waste mixture product of POs (*i.e.*, mixed according to the optimal mixing ratio). The ZSM-5 catalyst was used for the Set-2 experiments with the varying catalyst-to-plastic mass ratio (C:P) for the mixture of waste POs to compare non-catalytic and catalytic experiments. The CAT experiments were also performed under the same conditions as Set-1. The detailed process conditions of the Set-1 and Set-2 experiments are listed in Table 2.7 and Table 2.8, respectively.

2.3.3. Characterization Methods

2.3.3.1. Ultimate and Proximate Analysis

Ultimate analysis of individual waste plastics was performed in the CHN/S analyzer (Leco TruSpec CHN Analyzer). The oxygen content of the starting materials was determined by difference. Proximate analysis of the individual plastic wastes was determined in a muffle furnace (Protherm 160/9 muffle furnace). The moisture content, volatile matter, and ash content of exactly 1 g of each sample were determined according to the instructions in ASTM D 3173, ASTM D 3175, and ASTM D 3174, respectively. The fixed carbon content of the samples was determined by difference.
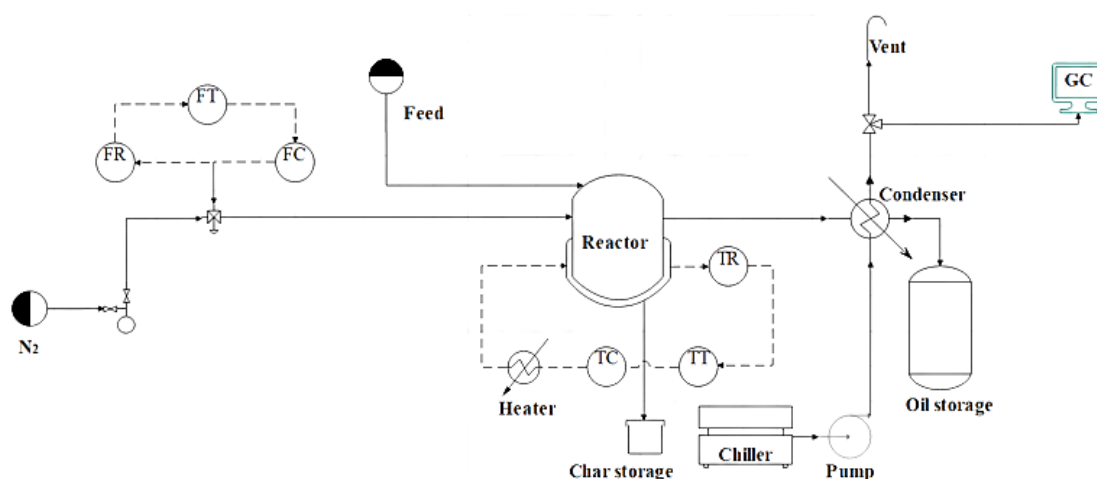
Figure 2.4. The experimental setup used for continuous pyrolysis of fresh and waste polyolefins.
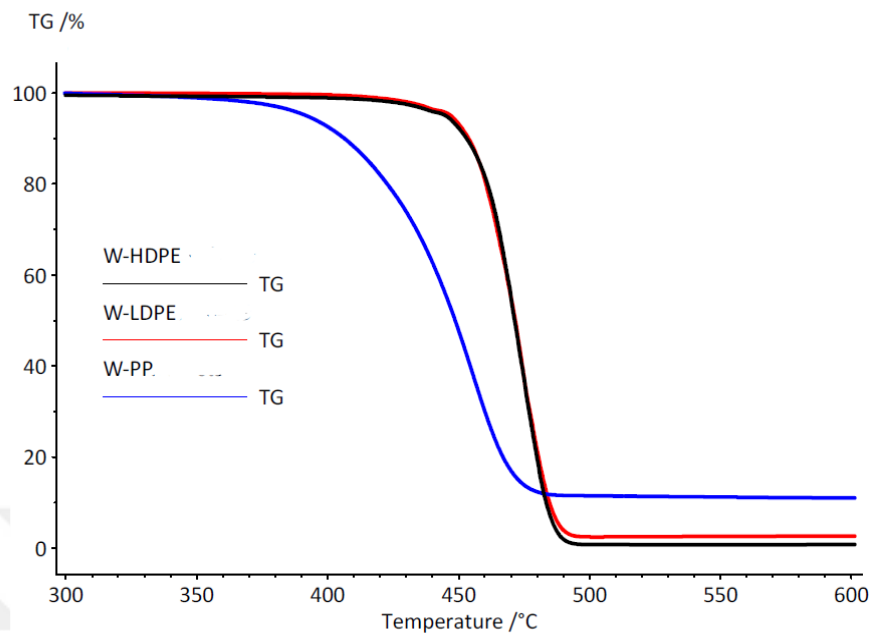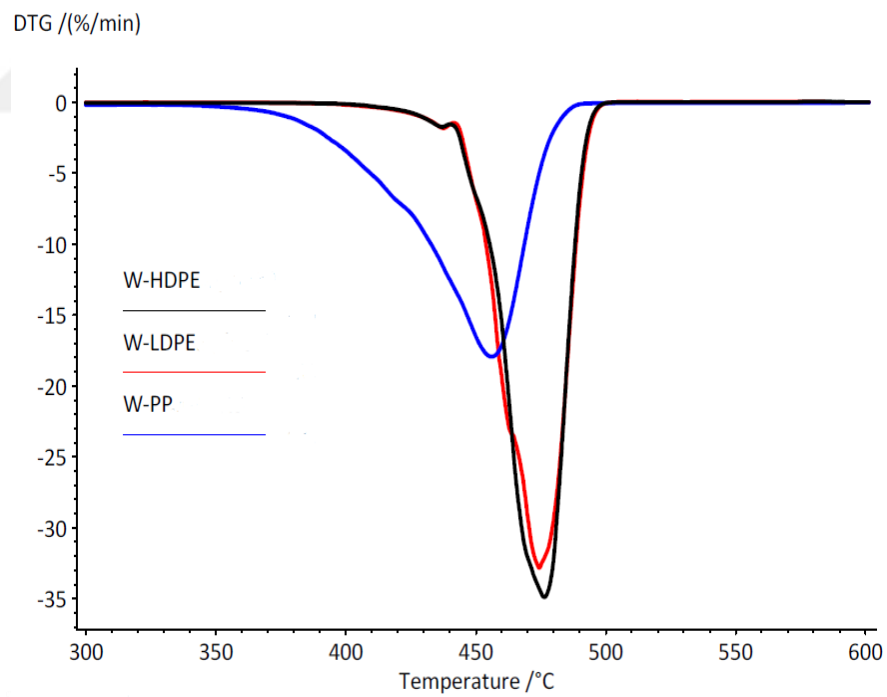
Figure 2.5. Results of thermal analyses for POs a) TGA, and b) DTG.

Table 2.11. The experimental conditions for Set-1 (non-catalytic experiments)

	F-HDPE	F-LDPE	F-PP	F-Mix	W-HDPE	W-LDPE	W-PP	W-Mix
Mixing ratio, (HDPE: LDPE: PP, *wt.%*)	100:0:0	0:100:0	0:0:100	25:25:50	100:0:0	0:100:0	0:0:100	25:25:50
Feed intake, g/min	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Temperature, °C	450	450	450	450	450	450	450	450
N_2 flow rate, L/min	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1
Process duration, min	60	60	60	60	60	60	60	60

Table 2.12. The experimental conditions for Set-2 (catalytic experiments).

	F-Mix	W-Mix	W-C60	W-C80	W-C100
Mixing ratio, (HDPE: LDPE: PP, *wt.%*)	25:25:50	25:25:50	25:25:50	25:25:50	25:25:50
Feed intake, g/min	1.5	1.5	1.5	1.5	1.5
Temperature, °C	450	450	450	450	450
N_2 flow rate, L/min	1.1	1.1	1.1	1.1	1.1
Process duration, min	60	60	60	60	60

2.3.3.2. Bomb Calorimeter

ASTM D5865 was followed for high heating value (HHV) measurements. Manually crushed plastic waste was pelletized before the analysis of HHVs in an oxygen bomb calorimetry (Parr 6300 Oxygen Bomb Calorimeter).

Higher heating values (HHV) of each liquid sample were measured by a bomb calorimeter (PRECYZJA-BIT, KL-12Mn) by flowing [105]. In a range of 0.6-1.2 g, the liquid samples were weighed with a precision balance (METLER TOLEDO, XS204) and loaded into the bomb calorimeter. The HHV determination of the analysis was repeated twice for each sample.

2.3.3.3. Thermal Gravimetry Analysis (TGA)

Thermogravimetry analysis system (NETZSCH, Libra 209 F1) was used to determine the maximum conversion efficiency and the maximum degradation temperatures for the individual plastic wastes and the waste mixture before the pyrolysis experiments. 12 ± 0.1 mg of plastic waste was weighed in a sensitive balance (METLER TOLEDO, XS204) and placed in ceramic crucibles. Samples were placed on a high-sensitivity c-DTA® with SiO2 coating as a sample carrier. Analyses were performed under a flow of 20 mL/min of high-purity nitrogen (99.999%). The samples were heated from 25 °C to 700 °C at a heating rate of 10 K/min. The derivative thermal gravimetry (DTG) curves were determined from the TGA curves.

2.3.3.4. Gas Chromatography-Mass Spectroscopy (GC-MS)

Gas chromatography coupled with a mass spectroscopy (GC-MS) system (Agilent 6890N/ 5973N EI Network MSD) was used to determine the composition of the liquid samples (*i.e.,* C_5-C_{40} hydrocarbon range). 1 µL of each sample was dissolved in a separate vial containing 50 µL of tetrahydrofuran (THF) solvent. The mixtures were shaken manually until homogeneity of the mixtures was achieved. The capillary column was HP -5ms (30 m length, 0.25 mm inner diameter, 0.25 µm film thickness). An autosampler whose syringe capacity is 10 µL, was used for each injection of 1 µL of each sample at

200 °C. Helium was used as the carrier gas, of which constant flow rate was applied at 1.1 mL/min. The temperature of the oven was initially 40 °C and was maintained for 2 minutes. Then the oven was heated to 200 °C with a heating rate of 3 °C/min. The temperature was increased by 200 °C to 320 °C with a heating rate of 5 °C/min and held constant at 320 °C for 10 minutes. The total run time was 89 minutes for each analysis. The NIST library was used to identify the compounds found in the liquid samples.

C_{21+} hydrocarbons are referred to in the literature as the "wax" fraction of the liquid of a plastic pyrolysis (Elordi et al. 2011; Salaudeen et al. 2021). The fraction consists of a highly viscous semisolid at room temperature that behaves like a Newtonian fluid in a hot water bath (about 100 °C). To analyze the liquid fraction of plastic pyrolysis, a suitable solvent with the ability to dissolve waxy hydrocarbons (*e.g.,* THF (Elordi et al. 2011), hexane (Zhao et al. 2020)) and a specific columns required (*e.g.,* HP 5ms (Salaudeen et al. 2021; Park et al. 2019), HT Inferno 2 (Kusenberg et al. 2022)) to detect waxy hydrocarbons. The flame ionization detector (FID) is often coupled with GC in the literature to detect all C-H bond-containing products in the analysis of pyrolysis liquids and to perform quantitative analysis (Frączak, Fabiś, and Orlińska 2021; Zayoud et al. 2022; Park et al. 2019). Quantitative analysis could not be performed for this study due to lack of methodology for GC-FID.

2.3.3.5. Gas Chromatography-Thermal Conductivity Detector (GC-TCD)

Gas chromatography coupled with a thermal conductivity detector (GC-TCD) system (Agilent 6890N) was used to monitor the non-condensable gas mixture including H2, CO, CO2, and C1-C3 hydrocarbons. The injection volume was 1 µl. The column (RESTEK, Shincarbon ST, 2 m long and has a 2 mm inner diameter) temperature was kept constant at 50 °C for 3 min. Then it was heated to 100 °C at a heating rate of 50 °C/min and held for 5 min. The temperature was raised to 200 with the same heating rate and kept constant at this temperature for 5 min. Then the GC oven was heated to 250 °C and kept at this temperature for 18 min.

CHAPTER 3

RESULTS OBTAINED FROM THE LITERATURE SURVEY

3.1.   Introduction

High-density polyethylene (HDPE), low-density polyethylene (LDPE), and polypropylene (PP) are grouped as polyolefins (POs), representing 65% of waste plastics (Abdy et al. 2022). POs are suitable plastic types for liquid fuel production via pyrolysis technology. The high C/H ratio of pure POs (*ca.* 6.6) makes them ideal feedstocks for producing liquid products with higher calorific values. When the results of the proximate analysis of pure POs are considered (Phyllis2 2022) it is seen that they are composed only of volatiles so that the pyrolysis of POs yields a maximized production of a liquid product while limiting the production of solid and gaseous by-products. The amount of energy that could be generated by burning POs equal to 10 wt.% of the amount fed to the process can meet the energy demand of the pyrolysis process (Dispons 2006). Thus, the pyrolysis of POs - as an energetically self-sufficient process - can simultaneously provide a renewable fuel and contribute to the reduction of non-recycled plastic waste. However, the high viscosity and low thermal conductivity of plastics limit heat transfer during pyrolysis. Therefore, the type of pyrolysis reactor, in addition to other process parameters (*e.g.,* reaction temperature, residence time) directly affects the quantity and quality of the products of POs pyrolysis (Czajczyńska et al. 2017).

The main product of thermal pyrolysis POs is wax. Although wax is a valuable product, it cannot be utilized as a fuel for conventional internal combustion engines without being upgraded. Upgrading wax requires additional process units (*e.g.,* feeders, pressurized reactors) and promoters (*e.g.,* steam, catalysts), creating additional CAPEX and OPEX. Limiting wax formation and increasing lighter fuel production are possible by establishing optimal operating parameters and units for non-catalytic pyrolysis. In the pyrolysis of POs, increasing the pyrolysis temperature favors the cracking of waxes into smaller hydrocarbons (*e.g.,* gasoline-like fuels, non-condensable gases) (M. Arabiourrutia et al. 2012). Another option is to increase the vapor residence time; many studies find that longer vapor residence times result in hydrocarbons with lower molecular

weights (Predel and Kaminsky 2000; Park, Jeong, and Kim 2019). To set an optimal pyrolysis temperature and a vapor residence time, the pyrolysis reactor should be adjustable. Batch and/or semi-batch reactors are often preferred for laboratory scale because of their ease of operation but are difficult to scale up. In contrast, continuously operated reactors such as continuously spouted bed reactors (CSBRs), rotating cone reactors (RCRs) and continuously stirred tank reactors (CSTRs) overcome mass and heat transfer limitations (Miandad et al. 2016) and are therefore well suited for scaling and use in large-scale processes.

3.2.   Pyrolysis of Polypropylene

In this part, published research articles focusing on continuous and non-catalytic pyrolysis of PP are reviewed. The goal is to find optimal conditions for process parameters and the most suitable reactor type to produce gasoline-like liquid fuels. At the same time, the other focus is on NC pyrolysis of PP, to find optimal conditions to produce C_5-C_{13} hydrocarbons without promoters such as catalysts or other upgrades. To understand the relationship between temperature, reactor type, and liquid yield, the maximum allowable pyrolysis temperature, and lowest yield were set to be 550 °C and 70 wt.%, respectively. The data matching the highest liquid production range were further analyzed to determine the residence time of the vapor in different types of reactors was also investigated. In this study, the literature reports addressing the results of PP pyrolysis obtained from non-catalytic and continuously operated pyrolysis systems are critically reviewed.

Figure 3.1 shows the correlation between liquid yield and pyrolysis temperature. At a temperature higher than 550 °C, liquid production decreases with increasing temperature, while gas production accelerates due to secondary reactions, regardless of reactor type (M. Arabiourrutia et al. 2012; Jin et al. 2018; R. Aguado et al. 2002). The compositions of the liquid products are listed in Table 1, except for the studies by Jin *et al.*(Jin et al. 2018), Fraczack *et al.*(Frączak, Fabiś, and Orlińska 2021), Kaminsky (Kaminsky 1991), and Walendziewski (Walendziewski 2005), for which no data are available. In the temperature range of liquid production (T ≤ 550 °C), the main product of pyrolysis oil is wax (M. S. Qureshi et al. 2020). The trend is consistent with our collected data, except for the continuous and non-catalytic pyrolysis data in CSTRs.

Leaving the hot pyrolysis vapors for more than one second improves the cracking of the wax and the production of light hydrocarbons, especially at temperatures above 500 °C (Predel and Kaminsky 2000).

CSTRs were operated at temperatures below than the temperature (*i.e.,* 470 °C) where the maximum degradation occurs according to DTG data mentioned above. Although the pyrolysis temperature were significantly low for CSTRs, the liquid yield were not lower than 90 wt.% (Frączak, Fabiś, and Orlińska 2021; Murata et al. 2002; Murata, Brebu, and Sakata 2010). All studies used an extruder to preheat PP before delivering to it CSTRs. The use of a pretreatment reactor boosted liquid yield by shortening the time to reach pyrolysis temperature, which prevented the production of byproducts (*e.g.,* char) generated by slow pyrolysis (Papari, Bamdad, and Berruti 2021). Gasoline range hydrocarbons were the product in CSTRs (see Table 3.1). The formation of lighter hydrocarbons is unusual for the non-catalytic pyrolysis of plastics at very low temperatures (~400 °C). This trend can be explained in two ways: 1) PP is a branched polymer and has a lower C-C bond-breaking energy compared to other plastics (*e.g.,* low density polyethylene, high density polyethylene), which allows for greater cracking even at lower temperatures (Peng et al. 2022). 2) Elevated vapor residence time can also lead to the formation of C_5-C_{12} hydrocarbons, but the authors have not provided data on vapor residence time (Frączak, Fabiś, and Orlińska 2021; Murata et al. 2002; Murata, Brebu, and Sakata 2010).

Vapor residence time was less than one second for CSBRs suppressing both gas and light oil (*i.e.,* C_5-C_{20} hydrocarbons) yields. Arabiourrutia *et al.* (M. Arabiourrutia et al. 2012) reported that the gasoline and diesel range hydrocarbon yields were increased when the pyrolysis temperature was increased from 450 °C to 500 °C. In contrast to the study by Arabiourrutia *et al.* (M. Arabiourrutia et al. 2012), Aguado *et al.* (R. Aguado et al. 2002) did not observe any change in the yield of hydrocarbons in the gasoline and diesel range at the same temperatures [52]. As can be seen in Table 3.1, a slight increase in vapor residence time leads to the production of C_5-C_{12} hydrocarbons.

Continuous flow reactors (CFRs) were continuously operated tubular reactors. The data obtained for CFRs were in the range of liquid formation in Figure 1. In all studies, an extruder operated at a temperature between 250 °C and 280 °C was used as the pretreatment reactor (Walendziewski 2005; N. Miskolczi et al. 2009; Norbert Miskolczi, Bartha, and Angyal 2006). Miskolczi *et al.* (Norbert Miskolczi, Bartha, and Angyal 2006) and Walendziewski (Walendziewski 2005) reported a liquid yield of 96 wt%. The almost

complete liquid production would be triggered by the above-mentioned pretreatment process. In contrast to other studies, Miskolczi *et al.* (Norbert Miskolczi, Bartha, and Angyal 2006) reported 52 wt.%, 3 wt.%, and 45 wt.% as liquid, gas, and solid yields, respectively. Although no process time was mentioned in the study, the pyrolysis time would not have been sufficient for this study, which resulted in a high amount of solid product.
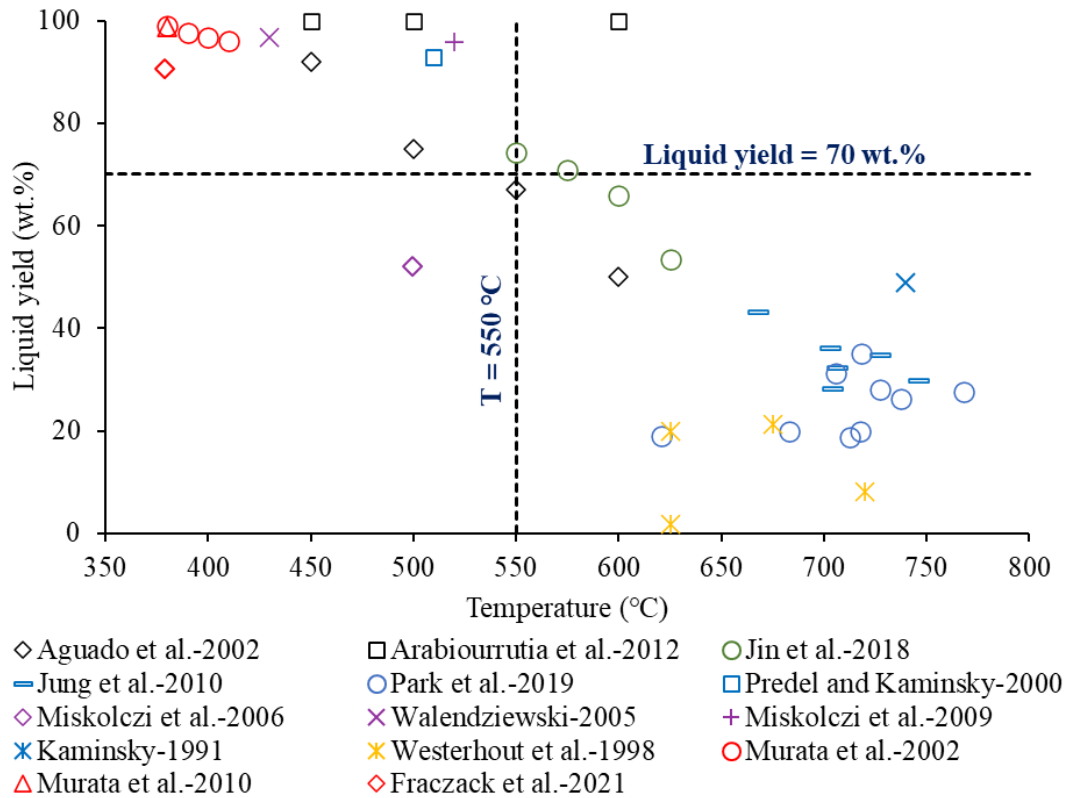
Figure 3.1. The correlation between liquid yield and pyrolysis temperature for PP
(**Black:** CSBR, **Red:** CSTR, **Blue:** BFBR, **Green:** FFR, **Orange:** RCR, **Purple:** CFR).

Bubbling fluidized bed reactors (BFBRs) (Park, Jeong, and Kim 2019; Jung et al. 2010; Kaminsky 1991), falling-film reactors (FFRs) (Jin et al. 2018), and RCRs (Westerhout et al. 1998b) were operated higher temperatures compared to other reactor types. Therefore, the data obtained for these reactors were placed in the gas formation section of Figure 1. Since these reactors, especially BFBRs and RCRs overcomes heat transfer limitations due to the use of heat transfer media (*e.g.,* sand), keeping the pyrolysis temperature in the liquid formation range and increasing the vapor residence time led to an improvement in gasoline-like oil production. For example, Predel and Kaminsky (Predel and Kaminsky 2000) studied the non-catalytic pyrolysis of PP in a BFBR at 510 °C, where the vapor residence time was about 5 s. In this study, 92 wt.% liquid and 30 wt.% C_5-C_{12} hydrocarbons were produced.

CSTRs were found to be the most efficient reactors to produce gasoline range (C_5-C_{12}) hydrocarbons at lower temperatures (~400 °C). It should be mentioned that the use of a pretreatment reactor for the hot plastic melt helps to obtain the highest yield of gasoline-like oil (54 wt.%). Although more than 90 wt.% liquid yield was obtained in CSBRs, the liquid product was almost all wax due to the immediate removal of vapors from the reactors. BFBRs, FFRs and RCRs were operated at gas production temperatures (T > 550 °C). These studies were good examples of gas production rather than gasoline production.

In this part, the literature reports dealing with the results of PP pyrolysis from non-catalytic and continuously operated pyrolysis systems are critically reviewed. At temperature higher than 550 °C, the yield of liquid product decreases. Using a heat carrier such as hot sand or pretreatment reactor to feed hot plastic to the main reactor enhances lightweight fuel production. CSTRs are found to be best performing reactors to produce gasoline-like fuel at temperatures below than 450 °C. The maximum C_5-C_{12} hydrocarbons yield was 54 wt.% obtained in CSTRs at 380°C. The main product in the pyrolysis oil was wax for CSBRs due to very short vapor residence time. In general, BFBRs, FFRs, and RCRs were operated at gas formation range (T > 550 °C).

Table 3.1. The composition of liquid products of the data point falling in temperature and yield boundaries.

Temperature (°C)	Vapor residence time (s)	Wax yield (wt.%)	Gasoline yield (wt.%)	Diesel yield (wt.%)	Total liquid yield (wt.%)	Ref.
450	0.020	92.0	0.00	0.00	92.0	[52]
500	0.020	75.0	0.00	0.00	75.0	[52]
550	0.020	67.0	0.00	0.00	67.0	[52]
450	0.054	92.0	1.10	6.90	100	[35]
500	0.054	75.0	3.30	21.7	100	[35]
510	5.60	56.2	28.8	6.40	91.4	[43]
510	4.20	57.5	31.1	6.48	95.1	[43]
520	NaN	48.9	28.9	18.0	95.8	[13]
380	NaN	13.4	54.3	32.4	100	[84]
380	NaN	13.2	54.2	32.5	100	[86]

NaN: Not a number

3.3. Pyrolysis of High-Density Polyethylene

This study compiles and investigates the literature reports addressing the results of HDPE pyrolysis obtained from non-catalytic and continuously operated pyrolysis systems. The ultimate goal of this part is to perceive the optimum process parameters for the maximized production of liquid products within the gasoline range (C_5-C_{12}).

Figure 3.2 shows that the pyrolysis temperatures higher than 600 °C resulted in an overall decrease in the liquid yield. At the same time, gas production was enhanced due to secondary cracking, independent of the reactor type (Lopez et al. 2017). Due to their allowance for elevated HDPE residence times, and their efficient heat transfer capabilities during pyrolysis, CSTRs are the best-performing reactors for gasoline range fuel production among the examined reactors for non-catalytic and continuous pyrolysis of HDPE. CSBRs were operated at higher temperatures compared to CSTRs (Murata et al. 2002; Murata, Brebu, and Sakata 2009b, 2010; Murata, Sakata, and Brebu 2022; Auxilio et al. 2017). The studies reported that wax is the main product. The trend can be

explained by the heat and mass transfer rates in the reactors. As seen in Fig. 1, BFBRs were operated out of the liquid product range compared to CSBRs (Lopez et al. 2017). Thus, gas production was the target for these experiments.

Figure 3.3 shows the effects of vapor residence time on gasoline range hydrocarbon and wax production in CSBRs and BFBRs. According to Figure 3.2, wax formation in pyrolysis oil decreases. In contrast, gasoline formation is enhanced by increased vapor residence time. Thermal pyrolysis of HDPE at 450 °C produces almost just wax in CSBRs since the temperature is lower than the maximum cracking temperature stated above. At this temperature, instant removal of hot vapors in less than 0.1 s from a CSBR is suitable for wax formation rather than gasoline production (R. Aguado et al. 2002; Elordi et al. 2011; M. Arabiourrutia et al. 2012; Miriam Arabiourrutia et al. 2017; Maite Artetxe et al. 2013; M. Artetxe et al. 2012; Ibáñez et al. 2014). Although increasing the temperature of pyrolysis from 450 °C to 500 °C or 550 °C converts 20 wt.% of wax to diesel range hydrocarbons; both increasing temperature and vapor residence time have an insignificant effect on the formation of C_5-C_{12} hydrocarbons. Pyrolysis of HDPE at 600 °C results in the highest yield of gasoline range hydrocarbons in CSBRs, but it is still not the optimum condition. CSBRs are known as suitable reactors for flash pyrolysis and provide flexibility for tailoring residence time. Thus, increasing residence time at lower temperatures provides a more economical process for gasoline production in CSBRs since vapor residence time is insufficient to crack further at this temperature. As the target product is generally gas for BFBRs, the reported pyrolysis temperatures and vapor residence times for BFBRs are higher compared to CSBRs. However, pyrolysis of HDPE in BFBRs at 650°C leads to more than 70 wt.% liquid yields and a significant amount of C_5-C_{12}, so BFBRs are also examined in this case concept. The optimum temperature and residence time for non-catalytic pyrolysis of HDPE for maximizing the yield of C_5-C_{12} hydrocarbons are 650 °C and 1 s, respectively. Residence times longer than a second in BFBRs causes excessive cracking of vapors so that the gas production is enhanced (Berrueco et al. 2002; F. J. Mastral et al. 2003; J. F. Mastral, Berrueco, and Ceamanos 2007). For instance, there is no significant difference in the gasoline yield at 650 °C for vapor residence times of 1 s and 2.6 s. However, a longer vapor residence time in the BFBR should not be allowed if a maximum liquid yield is aimed. On the other hand, no fair comparison can be developed for the reactors regarding vapor residence time due to the lack of information for CSTRs. But it should be known that the gasoline range hydrocarbon yield for CSTRs is reported between 36 wt.% and 60

wt.% which are higher than the yields obtained in the other reactors (*i.e.,* BFBRs and CSBRs).
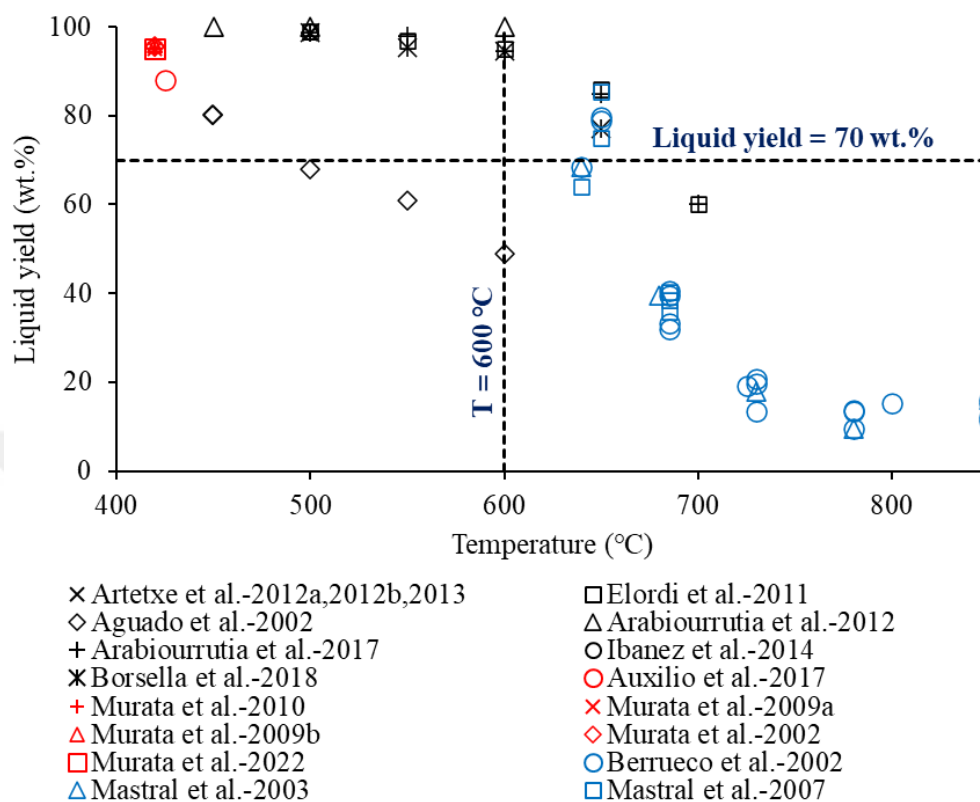
Figure 3.2. Liquid production from pyrolysis of HDPE in CSBR (black), CSTR (red), and BFBR (blue).
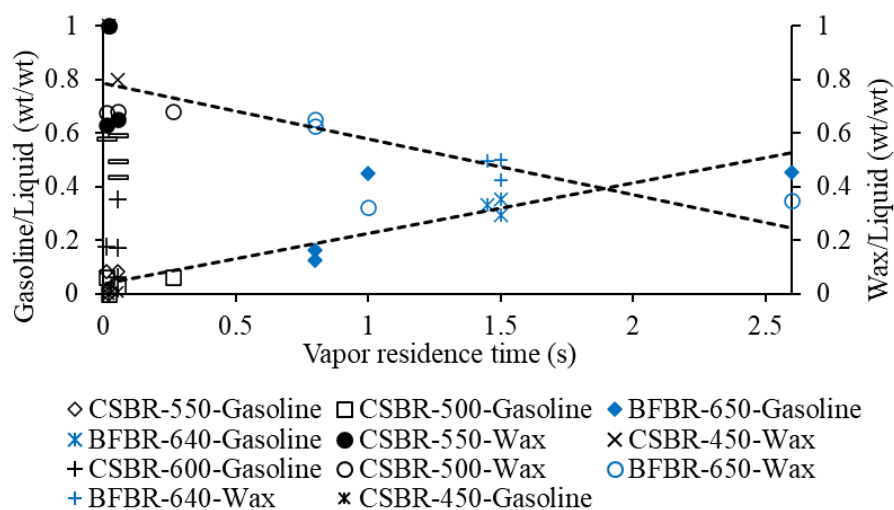
Figure 3.3. Effect of vapor residence time on liquid gasoline production in CSBRs (black) and BFBRs (blue)

Published articles reporting the results of pyrolysis of HDPE performed in non-catalytically and continuously operated systems were collected and further examined to determine the best-performing reactor type, optimum pyrolysis temperature, and vapor residence time that yields a maximization in the gasoline range (C_5-C_{12}) hydrocarbons. To give a detailed explanation for the optimum conditions for gasoline-like fuel production, vapor residence times are also investigated for the reactors except for CSTRs since no data is available in the data set. CSTRs are found to be the best-performing reactors for both liquid and gasoline production at lower temperatures (*ca.* 420 °C) compared to the operating temperatures CSBRs and BFBRs. The maximum optimal vapor residence of HDPE vapors in CSBRs is reported to be 0.05 s. CSBRs are suitable reactors for wax formation rather than lighter fuel production for all operating conditions. The data obtained in BFBRs are in the gas formation range. The temperature of 650 °C and a vapor residence time of 1 s are the optimum conditions for BFBRs and lead to the maximum gasoline yield (35 wt.%). CSTRs are highly recommended to produce hydrocarbons in the gasoline range (C_5-C_{12}) from HDPE because fewer wax forms and the C_5-C_{12} yield is higher under mild conditions.

3.4. Pyrolysis of Individual and Mixed POs

Pyrolysis of POs can be considered a self-sustained process in terms of its energy requirements. 280 MJ of energy per 100 kg POs is required for endothermic bond-breaking reactions (Dispons 2006). Gaseous products of pyrolysis (*i.e.,* non-condensable gases, NGC), composed of H_2 and C_1 to C_4 hydrocarbons, can fulfill and even exceed the energy requirements of pyrolysis of POs (Yang et al. 2022). Both the yield and the composition of the NGCs are essential to provide the required amount of energy for the process. The energy requirements of pyrolysis of POs can be met by changing process parameters such as increasing the vapour residence or decreasing the feeding rate, which will lead to enhanced gas yields (Elordi et al. 2011; N. Miskolczi et al. 2009). Although NCG yields of pyrolysis of PP reported in the works of Aguado *et al.* (R. Aguado et al. 2002) and Jin *et al.* (Jin et al. 2018) are very similar, the total energies of the NGCs produced in these studies are strikingly different. No H_2 yield was reported in Aguado *et al.* (R. Aguado et al. 2002)'s study, while Jin *et al.* (Jin et al. 2018) reported that the yield of H_2 varied between 0.2 wt.% and 1.7 wt.%. Since H_2 has the highest calorific value

among the NCGs, the total energies of tail gases of studies are remarkably separated (McAllister, Chen, and Fernandez-Pello 2011). Adjusting the quality and quantity of NCGs while maximizing the liquid yield of plastic pyrolysis can be accomplished with a process system that is operated at the optimum conditions. To produce fuel-like products from the non-catalytic pyrolysis of POs, the optimization of process units (e.g., feeder, reactor, and condenser types) and related operational parameters (*e.g.,* feeding rate, temperature, vapor residence time, pressure, etc.) are crucial. To resemble industrial processes, the design of a pyrolysis system should provide flexibility for optimization and favorableness for scaling up. Systems involving batch and/or semi-batch reactors are frequently preferred for lab-scale due to their ease of operation. However, they are challenging to be scaled up. In contrast, for the maximization of the yield and the quality of the targeted products, continuous systems, which are adjustable and easy to scale up, are preferred. On the other hand, reaction temperature has the biggest influence on the product distribution of pyrolysis. Many studies reported that elevated temperatures higher than the maximum cracking temperature for POs lead to the cracking of long-chain hydrocarbons to smaller ones favoring gas production, while the yield of liquids is diminished (Elordi et al. 2011; Milne, Behie, and Berruti 1999; Park, Jeong, and Kim 2019). Similarly, gas and liquid yields are directly proportional to vapor residence time. Secondary cracking reactions occur with increased vapor residence time that favors lighter products (*e.g.,* NCGs and gasoline-like hydrocarbons). When the main aim of pyrolysis is the maximization of liquid production, temperature and vapor residence time should be precisely optimized to produce liquid fuels while minimizing gas formation. In the study of Mastral *et al.* (J. F. Mastral, Berrueco, and Ceamanos 2007), increasing the residence time of the vapors of HDPE pyrolysis from 0.8 s to 2.6 s enhanced the yield of NGCs and gasoline-range hydrocarbons (C_5-C_{12}). Setting the temperature of the reactor to a moderate temperature (*i.e.,* 450 °C) and increasing vapor residence time can enhance production of lighter products (*e.g.,* light oils and NCGs).

Figure 3.4, based on the reported results in the literature, shows the correlation between the *pyrolysis temperature* and the *liquid yield* (*i.e.,* pyrolysis oil) obtained. As mentioned in Table 2.10, the highest degradation temperatures found by DTG for W-HDPE, W-LDPE, and W-PP were 477 °C, 473 °C, and 456 °C, respectively. Besides, the endset temperatures were found by TGA respectively as 501 °C, 495 °C, and 488 °C. The TGA and DTG results are in-line with the results reported in the related literature (Saad et al. 2021; Neves et al. 2007; Silva et al. 2020). For pyrolysis of POs as a mixture, the

maximum decomposition temperature decreases with an increasing PP content, while, on the contrary, a higher pyrolysis temperature (*e.g.,* 500 °C) is required with an increase in LDPE content (Frączak, Fabiś, and Orlińska 2021; Dubdub and Al-Yaari 2020; Chowlu, Reddy, and Ghoshal 2009). As shown in Figure 5, around 90 wt.% of liquid production is possible at 600 °C especially for HDPE due to its high activation energy for decomposition. Thus, 600 °C was selected to be the maximum temperature for the production of an optimal liquid yield in POs pyrolysis (shown as vertical dashed lines in Figure 5), although TGA and DTG data indicates a lower decomposition temperature (i.e T < 500 °C). Also, more than 90 *wt.*% of conversion of the initial mass of POs measured by TGA was reported in many studies (Neves et al. 2007; Silva et al. 2020; Chandrasekaran et al. 2015). Considering the thermal conversion efficiency, possible experimental errors, and the average yield in our database, 70 *wt.*% is set as the minimum liquid yield (shown as horizontal dashed lines in Fig. 5). The data falling in the optimal zone for liquid production (upper-left section of the chart) were further examined to explain the energy potential of the gas products (*i.e.,* C_1 to C_4 hydrocarbons) as by-products. The total combustion energy of the gases was calculated by Equation 1, where E_{gas} and CV are the total energy of gas products and the calorific value, respectively (McAllister, Chen, and Fernandez-Pello 2011).

According to Figure 3.4, the liquid yield decreases at temperatures higher than 600 °C where the gas formation is favored due to excessive cracking reactions taking place in the vapor phase regardless of the plastic type (Jin et al. 2018). At temperatures below 450 °C, which is lower than the highest degradation temperatures for POs (*i.e.,* 480 °C for HDPE, 470 °C for LDPE, 460 °C for PP, and 470 °C - 525 °C for mixed POs), more than 90 *wt.*% of liquid is obtained (Saad et al. 2021). Typically, at these temperatures, the produced liquid is in wax form (Abdy et al. 2022). However, using a pyrolysis reactor that could eliminate heat and mass transfer limitations (*e.g.,* conical spouted bed reactor), a pretreatment unit such as an extruder (Chandrasekaran et al. 2015), or increasing the vapor residence time (Serrano et al. 2001) leads to wax cracking and hence favoring the production of liquids involving lightweight hydrocarbons

The liquid yield data obtained from the studies of Del Remedio Hernandez *et al.* (Del Remedio Hernández, García, and Marcilla 2005) and Mastellone *et al*. (Mastellone et al. 2002) are in the liquid production range but the maximum liquid yields were reported as 5.16 wt.% and 2 wt.%, respectively. Also, these studies reported high amount of solid residues, of which the yields varied between 60 wt.% and 90 wt.% depending on

the reaction temperature. The very low liquid yields and high solid yields were unusual according to other studies. Reported process durations of the experiments in the works of Del Remedio Hernandez *et al.* (Del Remedio Hernández, García, and Marcilla 2005) and Mastellone *et al.* (Mastellone et al. 2002) were no longer than 20 minutes which is evidently insufficient neither for a complete conversion nor maximizing the liquid yields at temperatures below 600 °C. In contrast, the studies show that if the process duration is as short as 10-20 minutes for pyrolysis of POs, higher than 80 *wt.*% liquid yield and a complete conversion can be obtained at the gas production range (*i.e.,* T > 600 °C in Figure 5) for a very short vapor residence time (*i.e.,* less than a second) (Elordi et al. 2011; F. J. Mastral et al. 2003; José F. Mastral, Berrueco, and Ceamanos 2006).

Polyethylene (PE), represented with green marks in Figure 3, is pyrolyzed at the gas formation range. Also, the main component in the gas product was ethylene for these studies. Thus, these studies may target monomer recovery (*i.e.,* ethylene) from PE (Park, Jeong, and Kim 2019; Mastellone et al. 2002; Jung et al. 2010; Predel and Kaminsky 2000).

In Figure 3.4, the majority of the collected data obtained through the continuously operated non-catalytic pyrolysis of mixed POs are located in the upper-left corner (*i.e.,* liquid production area), except the studies reported by (Donaj et al. 2012) and (Westerhout et al. 1998b). The feedstock mixing ratio (*i.e.,* 66.6 wt.% PE and 33.3 wt.% PP) and process conditions took place for both studies resembles. However, the liquid yield obtained by Westerhout *et al.* (Westerhout et al. 1998b) is significantly lower compared to Donaj *et al.*'s (Donaj et al. 2012) work. The difference can be explained with the reactor types used in the studies. Rotating cone reactor is the reactor in the work of Westerhout *et al.* (Westerhout et al. 1998b) utilizing hot sand as heat carrier. The rotating cone reactor overcame more efficiently the heat transfer challenges than the bubbling fluidized bed reactor that was used by Donaj *et al.* (Donaj et al. 2012) so very low liquid yield was obtained at the gas formation range (*i.e.,* T > 600°C).

Based on the detailed gas compositions provided in the selected studies, the total energy required for the pyrolysis of POs (with 100 kg basis) was calculated by Equations (1.1) and (1.2) and given in Table 3.2. Both the yield and the composition of gas products are important for determining the energy required for pyrolysis. Gas yields of *ca.* 5 wt.% were found sufficient to provide almost all energy needed for the pyrolysis of POs. The elevated H_2 contents in the gas products lead to a decrease in the required total amount of gases (Kumagai et al. 2020). Thus, increasing the H_2 yield, in a well-optimized process,

will provide sufficient energy for the pyrolysis of POs without sacrificing the liquid yield.

Figure 3.5 shows the relation between H_2 production and pyrolysis temperature. At temperature higher than 600 °C, H_2 yield increased. The dehydrogenation reaction requires higher temperatures (*e.g.,* 600 °C) (Jung et al. 2010) so the data intensity in the right side of the Figure 6 is low. At liquid production range in Figure 5 (*i.e.,* T≤ 600 °C), some of the studies had enough energy for endothermic bond breaking as explained in Table 6. However, the work of Williams and Williams (P. T. Williams and Williams 1999) is the only study which reported the composition of NCGs containing H_2 due to elevated vapor residence time (*i.e.,* 15 s). Tailoring vapor residence time precisely at milder temperatures can also help to produce energetically sufficient NCGs for pyrolysis.
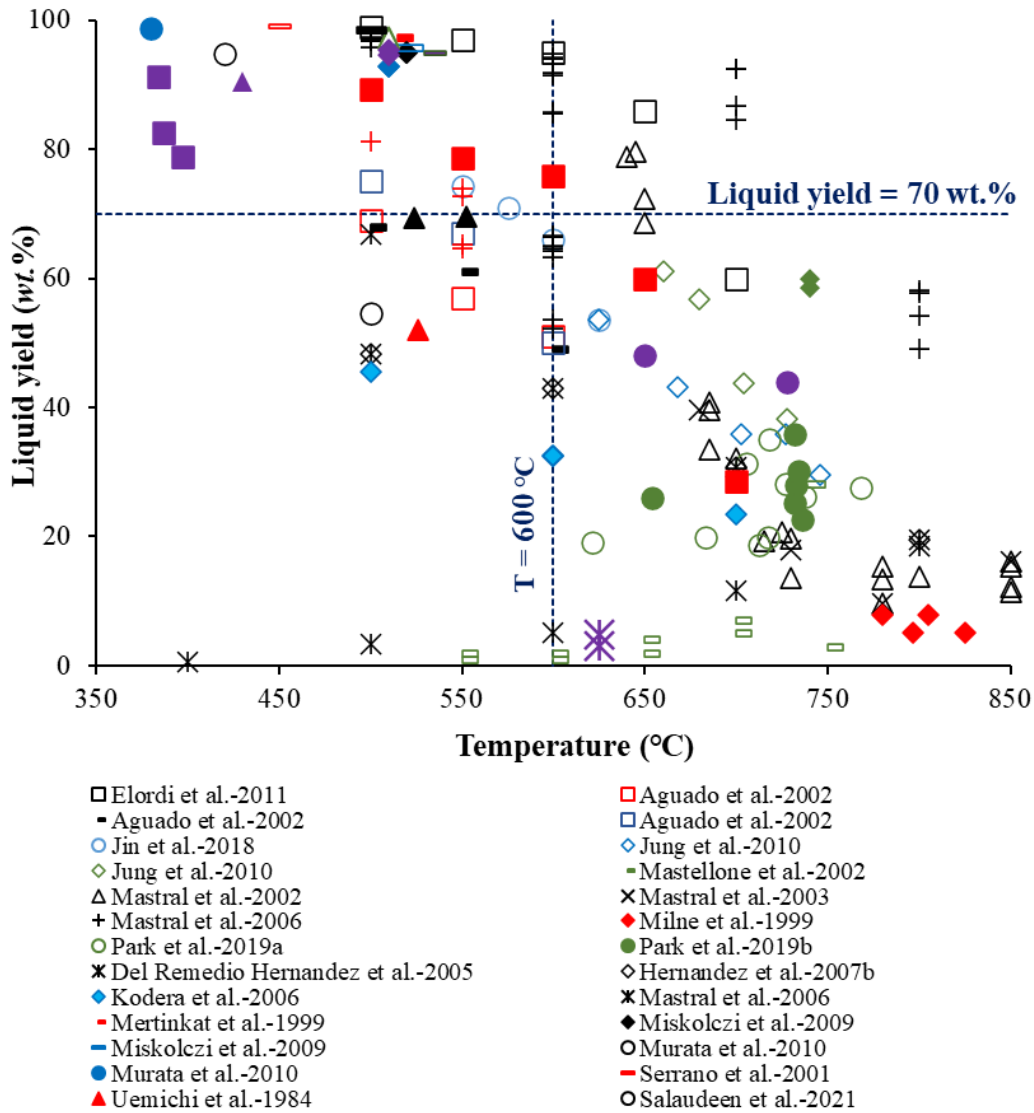
Figure 3.4. The correlation between the liquid yield and the pyrolysis temperature (**Black:** HDPE, **Red:** LDPE, **Blue:** PP, **Green:** PE, **Purple:** Mixed POs).

Table 3.2. The analysis of by-products of data (obtained at below 600 °C and yielded more than 70 wt.% of liquid) as an energy source for pyrolysis of POs.

Plastic Type	Liquid yield (*wt.%*)	Gas yield (*wt.%*)	% Energy provided by gases for pyrolysis of 100 kg POs	Ref.
HDPE	95-99	1-5	21-92	(Elordi et al. 2011)
HDPE	85.5-97	14.4-2.1	7-250	(José F. Mastral, Berrueco, and Ceamanos 2006)
HDPE	98.5	1.5	26	(Maite Artetxe et al. 2013)
HDPE	94.9	5.1	91	(N. Miskolczi et al. 2009)
LDPE	99	1	18	(Serrano et al. 2001)
LDPE	97.4	2.4	29	(Mertinkat et al. 1999)
LDPE	75.8-89.2	10.8-24.2	228-443	(Paul T Williams and Williams 1999)
PE	97.2-97.4	2.4-2.6	33	(Predel and Kaminsky 2000)
PP	75	25	164	(R. Aguado et al. 2002)
PP	95.8	4.2	74	(N. Miskolczi et al. 2009)
PP	92.9	6.9	104	(Predel and Kaminsky 2000)
Mixed POs	94.7-95.4	4.5-5.1	81.8-92.6	(Predel and Kaminsky 2000)
Mixed POs	94	5.1	87.6	(Norbert Miskolczi, Wu, and Williams 2016)
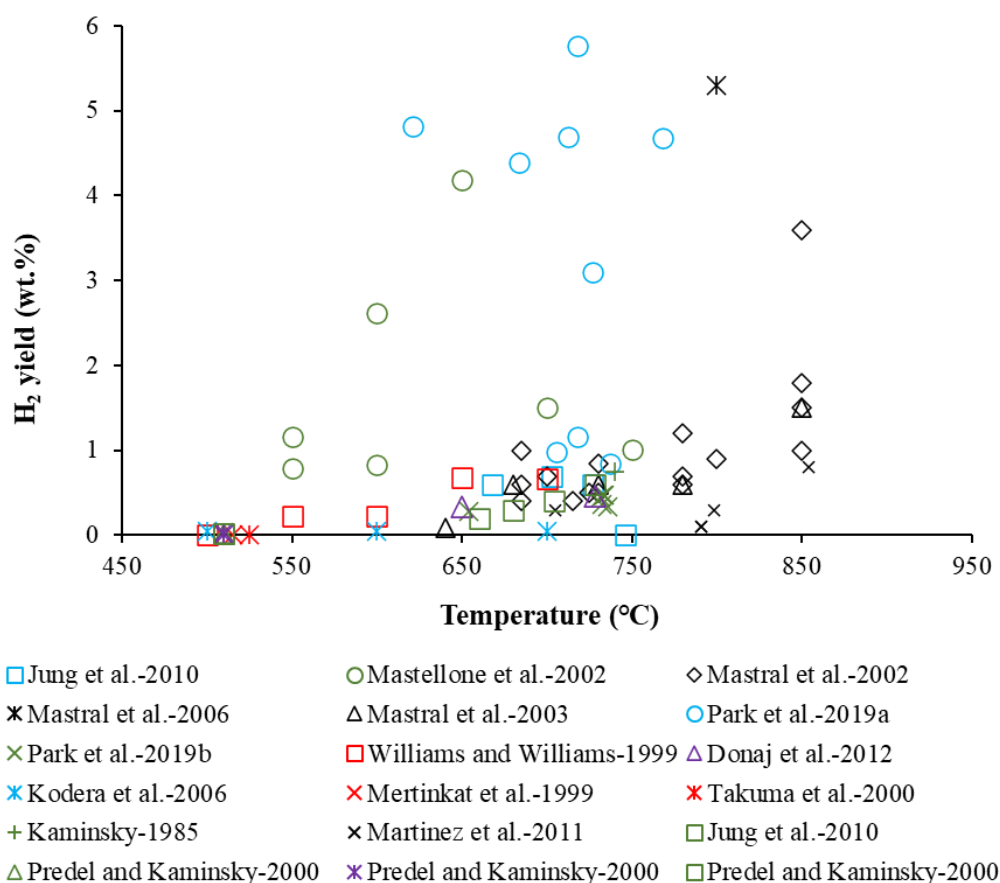
Figure 3.5. The correlation between H₂ yield and the pyrolysis temperature

(Black: HDPE, Red: LDPE, Blue: PP, Green: PE, Purple: Mixed POs).

3.3. Conclusions

Published articles reporting the results of pyrolysis of HDPE performed in non-catalytically and continuously operated systems were collected and further examined to determine the best-performing reactor type, optimum pyrolysis temperature, and vapour residence time that yields a maximization in the gasoline range (C_5-C_{12}) hydrocarbons. To give a detailed explanation for the optimum conditions for gasoline-like fuel production, vapour residence times are also investigated for the reactors except for CSTRs since no data is available in the data set. CSTRs are found to be the best-performing reactors for both liquid and gasoline production at lower temperatures (*ca.* 420°C) compared to the operating temperatures CSBRs and BFBRs. The maximum optimal vapour residence of HDPE vapours in CSBRs is reported to be 0.05 s. CSBRs are suitable reactors for wax formation rather than lighter fuel production for all operating conditions. The data obtained in BFBRs are in the gas formation range. The temperature of 650 °C

and a vapour residence time of 1 s are the optimum conditions for BFBRs and lead to the maximum gasoline yield (35 wt.%).

The literature reports dealing with the results of PP pyrolysis from non-catalytic and continuously operated pyrolysis systems are critically reviewed to explain the optimum process conditions. At a temperature higher than 550 ℃, the yield of liquid product decreases. Using a heat carrier such as hot sand or pretreatment reactor to feed hot plastic to the main reactor enhances lightweight fuel production. CSTRs are found to be best performing reactors to produce gasoline-like fuel at temperatures below 450 ℃. The maximum C_5-C_{12} hydrocarbons yield was 54 wt.% obtained in CSTRs at 380 ℃. The main product in the pyrolysis oil was wax for CSBRs due to the very short vapor residence time. In general, BFBRs, FFRs, and RCRs were operated at the gas formation range (T > 550 ℃).

The literature data shows that 90 wt.% of liquid yield can be obtained by non-catalytic pyrolysis of POs thanks to a suitable reactor, heat carrier and/or pretreatment reactor at milder temperatures. Also, *ca.* 5 wt.% of the gaseous product contains sufficient energy for the pyrolysis of POs.

CHAPTER 4

RESULTS OF DESIGNS OF EXPERIMENTS

4.1. Introduction

Thanks to their promising physicochemical properties, POs are widely used by many researchers as feedstock for pyrolysis to mimic petrochemical-based fuel oils [35,64,87,123]. The researchers designed their experimental plan in a conventional way: 1) selecting and characterizing a feedstock; 2) selecting process parameters in a range (*e.g.,* 450 ℃, 500 ℃, and 550 ℃ as pyrolysis temperature); 3) conducting experiments; 4) comparing results. The conventional approach limits researchers' understanding if they do not conduct all possible experiments according to their process parameters (*i.e.,* control factors) and their levels. For example, a set of experiments with 3 control factors and 4 levels for each factor contains 81 experiments for a complete understanding and comparison of conditions. On the other hand, only 9 experiments are required to optimize the process conditions using the Taguchi orthogonal array design. Using a DOE application for process optimization has several advantages. The number of experiments is limited, which saves significant time and money while minimizing variability in the results. Another advantage of using DOE is that you can obtain robust results while producing high-quality products. Considering the advantages of DOE, in this study Taguchi Method is used for experimental design.

4.2. Design of Experiments by Taguchi Method

4.2.1. Fresh LDPE Experiments

Nine experiments were performed according to Taguchi's L9 orthogonal array design for pyrolysis fresh LDPE to understand how pyrolysis parameters affect the

product yields, especially liquid yield, and conversion efficiency. Also, the order of importance was determined by using Minitab software to enlighten the next experiments. The mass balance of the nine experiments is shown in Table 4.3.

The optimal conditions are shown for the control factors of LDPE experiments in Figure 4.2. The optimal conditions giving the highest liquid yield for this set of experiments are 0.9 L/min (A1) as the N_2 flow rate, 15 min (B2) feeding period, 30 g (C3) as the plastic amount per feeding, and 0 ℃ (D3) as condensation temperature. The predicted liquid yield obtained at A1B2C3D1 conditions is 96.7 wt.%. Any confirmation experiment was performed for LDPE. No repeated runs for the experiments and no confirmation experiments were performed for LDPE. Thus, the validation of the model of LDPE is not proved.

LDPE experiments were not just designed to optimize the process conditions but to learn how the experimental set-up handled the plastic loading for varying feeding periods under constant N_2 flow. The operation temperature was also investigated for the efficiency of gas and liquid sample collection.

To maximize liquid yield by pyrolysis, fast pyrolysis conditions that include instant removal of hot vapors from a reactor are generally preferred (Anuar Sharuddin et al. 2016). However, the optimum N_2 flow rate was found as the lowest rate (0.9 L/min) for the same purpose for the LDPE experiments. TGA results show that pyrolysis of LDPE occurs at a temperature between 359 ℃ and 535 ℃ (Diaz-Silvarrey, McMahon, and Phan 2018; Saad et al. 2021). Also, LDPE has the second-highest activation energy of bond breaking (Dubdub and Al-Yaari 2020). In light of this information, increasing vapor residence time by decreasing the N_2 flow rate helps to enhance both conversion efficiency and liquid production.

10 min as the feeding period is not sufficient to pyrolyze all the loaded plastics per feeding. The conversion efficiency for 10 min increased by the increase in plastic amount per feeding. The unconverted plastic melt behaved like a heat carrier for the next feeding that limiting the temperature drop in the reactor, while the temperature could not be retained to the pyrolysis temperature, 450 ℃, before the next feeding resulted high amount of unconverted LDPE in the reactor. 15 min is the optimum condition with the highest conversion efficiency. 15 min was the optimum condition for the feeding period since it led to the complete conversion of LDPE and yielded 91.5 wt.% of liquid product. On the other hand, 20 min was also enough to pyrolyze LDPE almost completely. The

feeding period allowed hot vapors to stay more than enough, which caused an increase in gas yield.

Table 4.1. Mass balance obtained from Taguchi's experimental design for pyrolysis of LDPE.

|	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9
Temperature, ℃	450	450	450	450	450	450	450	450	450
N$_2$ flow rate, L/min	0.90	0.90	0.90	1.00	1.00	1.00	1.10	1.10	1.10
Feeding period, min	10	15	20	10	15	20	10	15	20
Plastic amount per period, g	10	20	30	20	30	10	30	10	20
Condenser temperature, ℃	0	-5	-10	-10	0	-5	-5	-10	0
Feed intake, g/min	1.00	1.33	1.50	2.00	2.00	0.50	3.00	0.67	1.00
Total plastic fed, g	60	80	90	120	120	30	180	40	60
Process duration	60	60	60	60	60	60	60	60	60
Liquid yield, wt.%	53.1	91.5	64.4	55.0	77.7	58.2	70.8	63.4	73.7
Gas yield, wt.%	4.9	8.5	25.2	23.6	20.6	35.1	16.1	35.3	25.8
Solid yield, wt.%	42.0	0.00	11.6	21.4	1.75	6.66	13.1	1.25	0.50
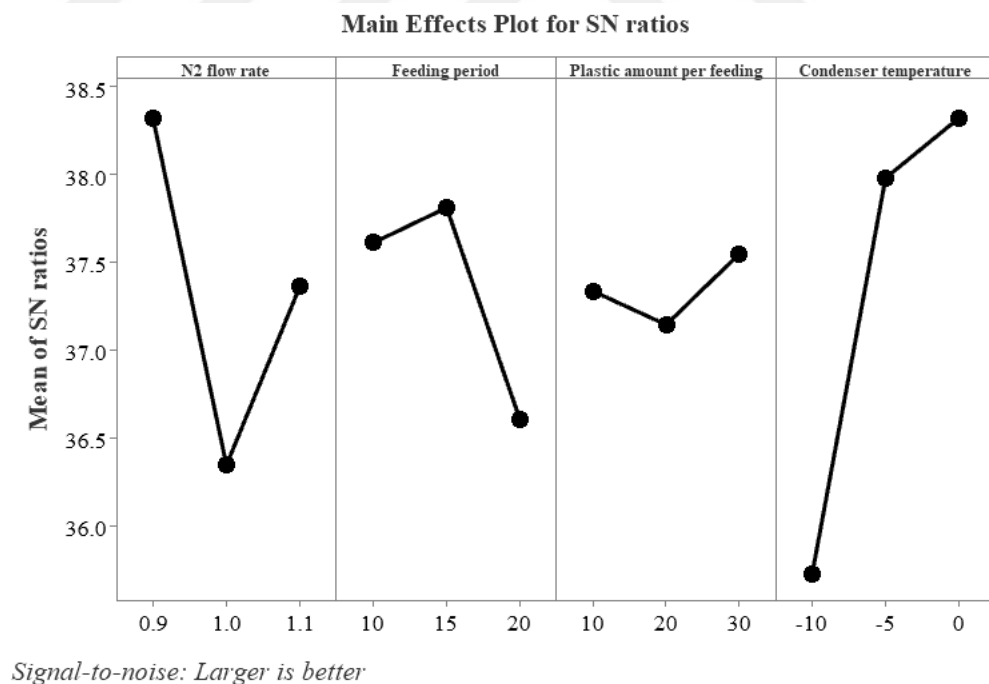
Figure 4.1. The optimum conditions of control factors for pyrolysis of fresh LDPE in the concept of "larger is better".

The plastic amount per feeding is directly related to feed intake. In general, an increase in plastic amount per feeding limits vapor movement, which means enhanced vapor residence time (K. M. Qureshi et al. 2018a). Similar to the N_2 flow rate trend, for this control factor, accelerated vapor residence time indicated more liquid production and conversion efficiency.

The condenser temperature is important to capture all condensable gases. If the condenser temperature is not sufficient to cool the hot gases swept from the reactor, condensable gases and permanent gases will be thrown away together, reducing the liquid product yield and distorting the product distribution. To determine the temperature of the condenser, the boiling points of the possible hydrocarbon ranges in the liquid product should be considered. The boiling points of gasoline, diesel, and wax hydrocarbons are < 220 °C (Vempatapu and Kanaujia 2017), < 360 °C (Elordi et al. 2011), and < 500 °C (Sultan Majed Al-Salem and Dutta 2021), respectively. For the setup used in this study, 0 °C (D1) is predicted to be the optimal condition for condensation that seems to be enough to cooldown hot vapor. However, problems due to condensed liquids in the outlet pipe occurred in almost all experiments. Lowering the condensation temperature lessened the cognition problem. Therefore, the operating temperature should be as low as possible for the effective separation of condensable and non-condensable gases. Another solution is to use a series of condensers with cross flow to speed up heat exchange.

The order of importance of control factors investigated for non-catalytic pyrolysis of LDPE is given in Table 4.4. According to the results, the order of importance for the control factors in decreasing order is Condenser temperature > N_2 flow rate > Feeding period > Plastic amount per feed. However, the order is not reliable due to several reasons: 1) The model is not valid because of no repetition of the experiments. 2) Condenser temperature among the other process parameters is the only parameter that has no effect pyrolysis part, or reaction part, so it cannot be the most important control factor.

Run 2 has the highest liquid yield (*ca.* 91.5 wt.%) among the experiments, while the predicted highest liquid yield is 96.7 wt.%. The experimental and theoretical liquid yields obtained from pyrolysis of LDPE at 450 ℃ are similar to the results obtained at the same temperature in several studies whose reported liquid yields are varied from 80 wt.% to 100 wt.% at 450 ℃ (J. Aguado et al. 2002; M. Arabiourrutia et al. 2012; Serrano et al. 2001). Increasing vapor residence time directly by changing the N_2 flow rate or indirectly increasing the feed intake for pyrolysis of LDPE is results in an increase in liquid yield (Zhao et al. 2020; Westerhout et al. 1998b, 1998a).

Table 4.2. Response Table for Signal to Noise Ratios (Larger is better) for fresh LDPE.

Level	N_2 flow rate, L/min	Feeding period, min	Plastic amount per feeding, g	Condenser temperature, ℃
1	38.3	37.6	37.3	35.7
2	36.4	37.8	37.2	38.0
3	37.4	36.6	37.6	38.3
Delta	1.97	1.20	0.40	2.59
Rank	2	3	4	1

4.2.2. Fresh PP Experiments

The experimental conditions and mass balances of nine experiments designed by Taguchi's L9 orthogonal array are shown in Table 4.5. Similar to LDPE experiments, the experiment set was performed to investigate the stabilized experimental conditions and produce the maximum amount of liquid product from non-catalytic pyrolysis of fresh PP. The deciding the experimental conditions for the PP set, the outcomes learned from the experiments of LDPE. For example, the third level of condenser temperature (D) was set to the lowest possible temperature (*i.e.,* -25 ℃) to prevent the cognition problem in the outlet pipe.

The detect the optimal conditions by Minitab software for maximum yield of liquid product, the "the larger better" concept was selected. According to results obtained from Minitab, which is represented in Figure 4.3, the maximum liquid yield (*ca.* 78.41 wt.%) can be obtained for 1.00 L/ min N_2 flow rate (A3), 20 min as feeding period (B3), 20 g as plastic loading per feeding (C2), and 0 ℃ (D1) as condenser temperature. The predicted conditions are the same as the conditions of Run 9. For the PP set, there is no need to perform additional confirmation experiments since the predicted and experimental yield, 78.4 wt.%, are same at A3B3C2D1 conditions. However, the model should be validated by repetition of the experiments.   Also,   the   order   of importance calculated by the difference of S/N ratios in decreasing order is the plastic amount per feeding > feeding period > N_2 flow rate > condenser temperature (see Table 4.6).

The relation between liquid yield, N_2 flow rate and feed intake for PP experiments is very different from the experiments of LDPE. In contrast to LDPE, decreasing vapor residence time through increasing the flow rate of the inert gas and feed intake elevates the conversion efficiency and elevates the liquid yield for PP. The maximum liquid yield obtained for PP is significantly lower than the LDPE. The trend can be explained by the reaction speed of plastics. PP's pyrolysis reactions occur faster than LDPE's due to the lower activation energy of PP (Dubdub and Al-Yaari 2020; Chowlu, Reddy, and Ghoshal 2009).

Plastic amount per feeding and feeding period which are selected to control feed intake are the first and the second important control factors, respectively. 30 g PP feeding to the reactor at any frequency is resulted in high amount of solid residue (unconverted PP). Since PP was fed to the reactor at the ambient temperature (*ca.* 20°C), the temperature of the reactor could drop to around 270 °C. Before the next feeding, the reactor could not reach the pyrolysis temperature since the reactor has no instant heating and control mechanism. Reheating the reactor diminished the conversion efficiency of PP and liquid yield. Similarly, 20 g PP was not completely also pyrolyzed in short feeding periods, while 10 g PP is too less amount of plastic to deal with in any frequency of feeding that resulted in the fast decomposition of PP and can allow additional cracking of condensable hot vapors that reduces liquid yield.

Table 4.3. Mass balance obtained from Taguchi's experimental design for pyrolysis of fresh PP.

	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9
Temperature, ℃	450	450	450	450	450	450	450	450	450
N_2 flow rate, L/min	0.80	0.80	0.80	0.9	0.9	0.9	1.00	1.00	1.00
Feeding period, min	10	15	20	10	15	20	10	15	20
Plastic amount per period, g	20	30	10	10	20	30	30	10	20
Condenser temperature, ℃	-25	0	-12.5	0	-12.5	-25	-12.5	-25	0
Feed intake, g/min	2.00	2.00	0.50	1.00	2.00	1.50	3.00	0.67	1.00
Total plastic fed, g	120	120	30	60	80	90	180	40	60
Process duration	60	60	60	60	60	60	60	60	60
Liquid yield, wt.%	63.2	62.2	69.2	67.3	71.5	66.8	58.7	73.6	78.4
Gas yield, wt.%	15.2	18.0	30.5	24.5	23.2	19.5	18.0	24.2	20.6
Solid yield, wt.%	21.6	19.8	0.33	8.15	5.24	3.03	23.3	2.25	1.00

An instant removal of hot vapors preventing secondary cracking is another solution for maximizing liquid yield for pyrolysis of PP. Run 4 and Run 9 were conducted at very similar conditions except for the N_2 flow rate. The highest liquid yield was obtained for Run 9 which was a shorter vapor residence time than Run 4. Also, the studies reported using a high N_2 flow rate (*e.g.,* 11 L/min) lead to more than 90 wt.% of liquid yield for pyrolysis of PP (M. Arabiourrutia et al. 2012; R. Aguado et al. 2002). However, the maximum N_2 flow rate for the pyrolysis of PP for a stable process is 1.0 L/min.

The optimal condenser temperature, 0 ℃, is same as the LDPE's experiments for PP. Since PP has a more branched structure compared to LDPE (Anene et al. 2018), it leads to lighter hydrocarbons so the cognition problem due to the accumulation of waxy products in the outlet pipe rarely occurred for pyrolysis of PP. The stability of the setup and the validity of product distribution, keeping the condenser temperature as low as possible is also recommended for non-catalytic pyrolysis of PP.
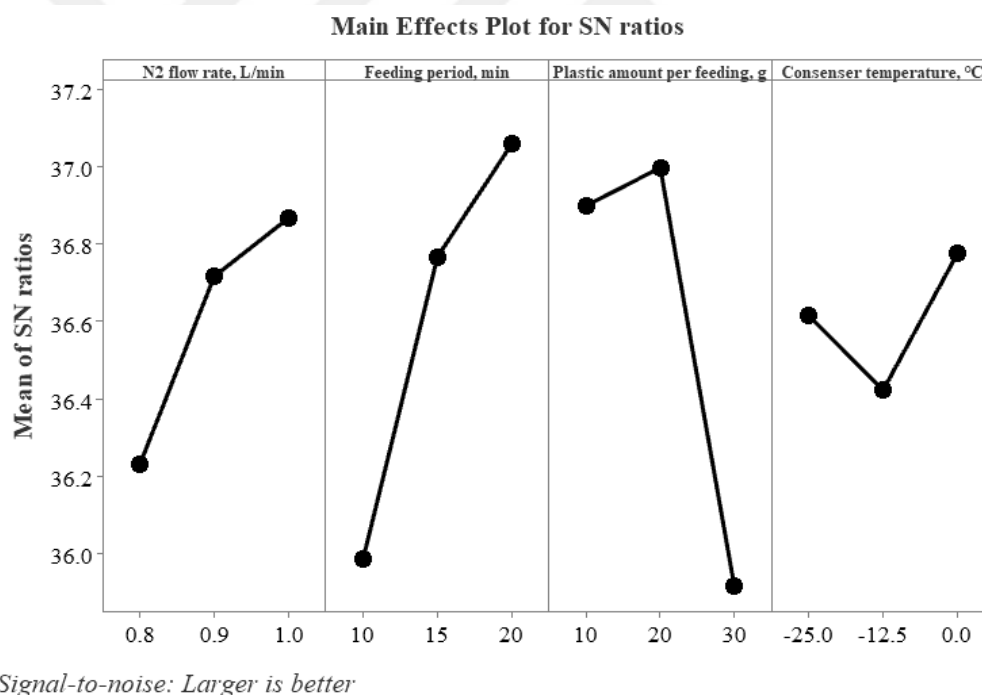
Figure 4.2. The optimum conditions of control factors for pyrolysis of fresh PP in the concept of "larger is better".

Table 4.4. Response Table for Signal to Noise Ratios (Larger is better) for fresh PP.

Level	N$_2$ flow rate, L/min	Feeding period, min	Plastic amount per feeding, g	Condenser temperature, °C
1	36.2	36.0	36.9	36.6
2	36.7	36.8	37.0	36.4
3	36.9	37.1	35.9	36.9
Delta	0.64	1.07	1.08	0.35
Rank	3	2	1	4

4.2.3. Fresh Mix Plastics Experiments

The operating conditions and mass balance for fresh mixed plastics are shown in Table 4.7.

The results of the pyrolysis of the individual fresh plastics were used to plan the optimization experiments of the fresh mixed plastics. As can be seen in Table 4.8, a larger S/N ratio means a higher liquid yield. Based on the S/N ratios of nine experiments, the optimum values for the control factors of pyrolysis of mixed fresh plastics were calculated and shown in Figure 4.4. The optimal conditions for the series of experiments are 1.1 L/min as the N$_2$ flow rate (A3), 1.5 g/min for feed intake (B2), and Mix-3 as the mixing ratio. 74.1 wt.% of liquid yield was predicted by the Minitab software and the confirmation experiments gave 73.3 wt.% of liquid for the optimal conditions of the control factors. The error of -3.6% between the experimental and predicted results of the confirmatory tests indicates that the model is reliable.

Increasing the N$_2$ flow rate increases liquid production. The N$_2$ flow rate is directly related to the vapor residence time, which is the second most important process parameter after temperature. The shortest possible residence time of the vapor in the reactor prevents secondary cracking reactions. Fast and flash pyrolysis favors a liquid product, which is consistent with the results of control factor A (N$_2$ flow rate) (Yildiz, Ronsse, and Prins 2017).

Table 4.5. Mass balance for optimization experiments and the confirmation experiment (CE).

	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	CE
Temperature, °C	450	450	450	450	450	450	450	450	450	450
N$_2$ flow rate, L/min	0.90	0.90	0.90	1.00	1.00	1.00	1.10	1.10	1.10	1.10
Mixing ratio	Mix-1	Mix-2	Mix-3	Mix-3	Mix-2	Mix-1	Mix-2	Mix-3	Mix-1	Mix-3
Feeding period, min	15	15	15	15	15	15	15	15	15	15
Plastic amount per period, g	15.0	45.0	22.5	15.0	45.0	22.5	15.0	45.0	22.5	45.0
Feed intake, g/min	1.0	3.00	1.50	1.0	3.00	1.50	1.0	3.00	1.50	1.5
Total plastic fed, g	60	180	90	60	180	90	60	180	90	90
Process duration	60	60	60	60	60	60	60	60	60	60
Liquid yield, wt.%	49.5	43.4	56.2	68.4	40.4	59.0	68.5	56.5	71.8	73.3
Gas yield, wt.%	19.9	12.6	17.1	24.7	12.1	20.3	24.7	13.9	20.5	21.6
Solid yield, wt.%	30.6	44.0	26.7	6.74	47.5	20.7	6.83	29.7	7.78	2.22

Increasing feed intake from 1.0 g/min to 1.5 g/min has a small effect on liquid product yield while increasing feed intake to 3.0 g/min results in a large decrease in liquid production. High feed intake suppresses vapor movement in a reactor that is resulted in high vapor residence time (K. M. Qureshi et al. 2018b). Since the operating temperature is lower than the maximum degradation temperature of POs determined by DTG, increasing vapor residence time carefully can be a good solution to crack heavy hydrocarbons(C_{21+}) and enhance the conversion efficiency of feedstocks. However, 3.0 g/min as the highest feed intake in this set of experiments is not appropriate for maximizing liquid production. Since the plastic mixture was not thermally pretreated before feeding, the temperature of the reactor decreased differently depending on the amount of feed. For example, at an N$_2$ flow rate of 0.9 L/min, the temperature of the reactor dropped to 330 °C at feed rates of 1.0 g/min (Run 1) and 1.5 g/min (Run 2), while 278 °C was the average temperature of the reactor measured immediately after each feed. On the other hand, the conversion efficiency of the experiments using 3.0 g/min was

significantly lower than other feeding rates, regardless of the other control factors. Thus, 15 min as a feeding interval was not sufficient to pyrolyze the entire feed for 3.0 g/min.

Mix-3 (C3) has the highest S/N ratio. Comparing the S/N ratio of Mix-3 and Mix-1, we can see that there is no significant difference. 35.6 and 35.5 are the S/N ratios of Mix-3 and Mix-1, respectively. The results show that the production of liquid is favoured when the plastic blend is mainly HDPE or PP. The samples containing 50 wt.% LPDE were not fully pyrolyzed and resulted in a high percentage of solid residues. For this reason, Mix-2, which consists mainly of LDPE, has a significantly lower S/N ratio. The experimental results can be explained by the synergistic effect between POs, which has been studied by many researchers. In the studies, it was reported that LDPE causes a slower reaction and increases the activation energy of bond breaking (Chowlu, Reddy, and Ghoshal 2009; Dubdub and Al-Yaari 2020). Since PP has lower stability due to the third carbon in its monomer, resulting in lower bond-breaking activation energy, increasing the PP content of a POs blend lowers the pyrolysis temperature (Frączak, Fabiś, and Orlińska 2021; Dubdub and Al-Yaari 2020; Chowlu, Reddy, and Ghoshal 2009).

On the other hand, the order of importance on liquid yield based on S/N ratios was calculated and is given in Table 4.9. Feed intake (B) is the most important factor while mixing ratio (C) has the least effect on the target product yield. The mixing ratio is found as the least important control factor affecting product distribution. Pyrolysis temperature is the most process parameter and the reactor temperature should be kept at the desired temperature while uniform heat transfer should be provided during pyrolysis to ensure the maximization of the target product. The relationship between feed intake and temperature drop in the reactor discussed above is proven in the order of concept, too. N_2 flow rate controls the vapor residence time during pyrolysis to prevent excessive cracking reactions. Although the mixing ratio has the least effect compared to other control factors, it should be remembered that the composition of the mixture is directly related to the quality of the products. As an example, PP-rich POs mixtures lead to more branched and cyclic compounds in the liquid products than linear compounds which are being triggered by HDPE and LDPE, while PS addition to POs mixture improves the yield of aromatic hydrocarbons (*e.g.,* benzene, toluene, and xylene) (Frączak, Fabiś, and Orlińska 2021).

Table 4.6. Liquid yields based on experimental results of Taguchi's L9 orthogonal array
design.

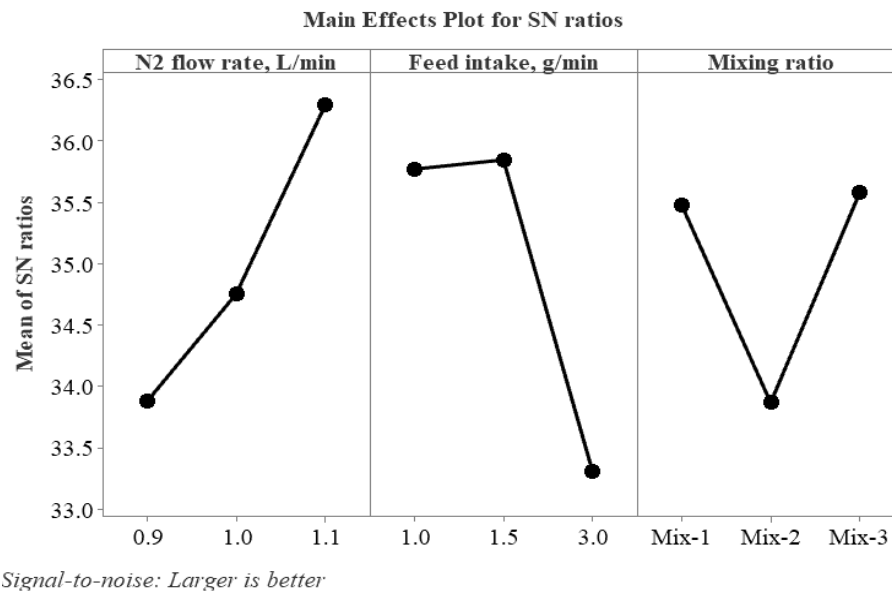| Run	N_2 flow rate, L/min	Feed intake, g/min	Mixing ratio	Liquid Yield, wt.%	S/N ratio
1	0.9	1	Mix 1	49.5	33.9
2	0.9	3	Mix 2	43.4	32.8
3	0.9	1.5	Mix 3	56.2	35.0
4	1.0	1	Mix 3	68.4	36.7
5	1.0	3	Mix 2	40.4	32.1
6	1.0	1.5	Mix 1	59.0	35.4
7	1.1	1	Mix 2	68.5	36.7
8	1.1	3	Mix 3	56.5	35.0
9	1.1	1.5	Mix 1	71.3	37.1
CE [predicted]	1.1	1.5	Mix-3	74.1	37.8
CE [experimental]	1.1	1.5	Mix-3	73.3	37.3

CE: Confirmation experiment

Figure 4.3. The optimum conditions of control factors for pyrolysis of mix fresh plastics
in concept of "larger is better".

Table 4.7. Response Table for Signal to Noise Ratios (Larger is better) for fresh mix plastics.

Level	N_2 flow rate, L/min	Feed intake, g/min	Mixing ratio
1	33.88	35.77	34.38
2	36.29	33.31	34.96
3	34.75	35.84	35.58
Delta	2.41	2.53	1.19
Rank	2	1	3

4.3. Conclusions

In this part, Taguchi's L9 orthogonal array design was used to optimize pyrolysis conditions for fresh LDPE, PP, and mixed POs. N_2 flow rate, feeding period, plastic amount per feeding, and condenser temperature were investigated as factors affecting pyrolysis conditions for LDPE and PP. The factors affecting the pyrolysis of mixed POs were N_2 flow rate, feed intake, and mixing ratio.

0.9 L/min (A1) as N_2 flow rate, 15 min (B2) feeding period, 30 g (C3) as the plastic amount per feeding, and 0 °C (D3) as condensation temperature were the predicted optimal pyrolysis conditions for LDPE. At the optimum conditions, 96.7 wt.% of liquid production was calculated. Condenser temperature was found to be the most important factor, followed by N_2 flow rate, feeding period, and plastic amount per feeding. Based on the observations during the experiments and the lack of validity of the model, the condenser temperature cannot be the most important factor affecting liquid yield.

The maximum liquid yield (*ca.* 78.41 wt.%) can be obtained at an N_2 flow rate of 1.00 l/min (A3), a feeding time of 20 min (B3), a plastic amount of 20 g per feeding (C2), and a condenser temperature of 0 °C (D1) for the pyrolysis of PP. The order of importance, calculated by the difference of S/N ratios in decreasing order, is the plastic amount per feeding > feeding period > N_2 flow rate > condenser temperature. It should be noted that the model has not been validated for PP either.

The optimal conditions for the experimental series are 1.1 L/min as N2 flow rate (A3), 1.5 g/min for feed intake (B2), and Mix-3 (25:25:50; HDPE: LDPE: PP) as mixing ratio. 74.1 wt.% liquid yield was predicted by using Minitab software, and confirmatory experiments yielded 73.3 wt.% liquid for the optimal control factor conditions. -3.6% of

error between theoretical and experimental liquid yield proves the validity of the model for pyrolysis of mixed POs.

CHAPTER 5

PYROLYSIS OF FRESH AND WASTE POLYOLEFINS AND UTILIZING NONCONDENSABLE GASES AS AN ENERGY SOURCE

5.1. Introduction

Under optimal process conditions, pyrolysis of polyolefins (POs) can yield as much as 90 *wt.*% of liquid product, *i.e.,* a combination of light oil fraction and heavier wax in different proportions. In the related literature, both the mixtures and individual types of POs were tested with an effort to maximize the quality and quantity of pyrolysis oils. Adjusting the composition of individual compounds in NCGs while maximizing the liquid yield of the pyrolysis of POs can, on the other hand, be accomplished with a system operating at the optimum process conditions. Steering various process parameters, *e.g.,* increasing the vapor residence time or decreasing the feeding rate, may lead to enhanced gas yields (Elordi et al. 2011; N. Miskolczi et al. 2009). In the work of Dispons (Dispons 2006), the energy required for the endothermic bond-breaking reactions for POs is reported to be 2.8 MJ/kg. Gaseous products of pyrolysis (*i.e.,* NCGs), composed of H_2 and C_1 to C_4 hydrocarbons, can fulfill and even exceed the energy requirements of pyrolysis of POs (Yang et al. 2022), making it a self-sustaining process in terms of its energy requirements. The higher heating values of individual components of NCGs are 141.7 MJ/kg, 55.5 MJ/kg, 50.3 MJ/kg, 51.9 MJ/kg, 45.8 MJ/kg, 50.3 MJ/kg, 45.3 MJ/kg and 49.5 MJ/kg for H_2, CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, C_4H_8 and C_4H_{10}, respectively (McAllister, Chen, and Fernandez-Pello 2011; chemeurope.com 2022). Among the individual components of NCGs, H_2 has the highest calorific value with *ca.* 141.72 MJ/kg (McAllister, Chen, and Fernandez-Pello 2011). In the works of Aguado *et al.* (R. Aguado et al. 2002) and Jin *et al.* (Jin et al. 2018), the NCG yields of PP pyrolysis are very similar with 25 *wt.*% and 28 *wt.*%, respectively. However, as mentioned in Table S1 (in the Supporting Information), the calorific values of the NGCs (*i.e.,* 164 kJ and 1592 kJ) produced in these studies are strikingly different due to the absence of H_2 in the work of

Aguado *et al.* (R. Aguado et al. 2002), while Jin *et al.* (Jin et al. 2018) reported that the yield of H_2 varied between 0.2 *wt.*% and 1.7 wt.%.

Reaction temperature has the biggest influence on the product distribution of the pyrolysis of plastics. Many studies reported that elevated temperatures higher than the optimum cracking temperature for POs (*i.e.,* 450 °C - 480 °C) (Diaz Silvarrey and Phan 2016; Dubdub and Al-Yaari 2020; Chowlu, Reddy, and Ghoshal 2009; Saad et al. 2021) lead to the cracking of long-chain hydrocarbons to smaller ones that favor gas production, while the yield of liquids is diminished (Elordi et al. 2011; Milne, Behie, and Berruti 1999; Park, Jeong, and Kim 2019). Similarly, gas and liquid yields are directly proportional to the vapor residence time applied; secondary cracking reactions favoring lighter products (*e.g.,* NCGs and gasoline-like hydrocarbons) occur with increased vapor residence times (Elordi et al. 2011; Abbas-Abadi et al. 2022). When the main aim of pyrolysis is the maximization of liquid production, temperature and vapor residence time should be precisely optimized to produce liquid fuels while minimizing gas formation. The studies showed that liquid product recovered from POs was composed mainly of C_{21+} hydrocarbons (> 90 wt.%) if the vapor residence time is shorter than 1 s at milder temperatures (*e.g.,* 450 °C), while longer chain hydrocarbons were broken to lighter hydrocarbons at higher temperatures (*i.e.,* 500 °C and 550 °C) (R. Aguado et al. 2002; M. Arabiourrutia et al. 2012). Thanks to the short residence time, secondary cracking reactions were prohibited so 8 wt.% of gas yield and no gas formation were reported by (R. Aguado et al. 2002) and (M. Arabiourrutia et al. 2012), respectively. In the study of (J. F. Mastral, Berrueco, and Ceamanos 2007), increasing the residence time of the vapors of HDPE pyrolysis from 0.8 s to 2.6 s enhanced the yield of NCGs and gasoline-range hydrocarbons (C_5-C_{12}) [12]. Similarly, gasoline-range hydrocarbon production increased from 40 wt.% to 50 wt.% for pyrolysis of LDPE when the vapor residence time is gradually increased from 12 s to 18 s (Zhao et al. 2020). Setting the temperature of the reactor to a moderate one (*i.e.,* 450 °C) and increasing vapor residence time can enhance the production of lighter products (*e.g.,* lighter oil fractions and NCGs).

This chapter aims to give a perspective on the continuously operated and energetically autonomous pyrolysis of POs by using experimental data generated by our research group. The effect of feeding rate, inert gas (*i.e.,* N_2) flow rate and the process duration on the product distribution of non-catalytic pyrolysis POs is investigated. The composition of gaseous products and their total energy contents were considered from the perspective of energy supply from the tail gases of the process. The ultimate goal is to

determine the optimum process parameters that maximize the liquid yield of pyrolysis of POs and investigate the suitability of NCGs as energy sources for the process.

5.2. Results and Discussion

Figure 5.1 shows the mass balances of the experiments performed with fresh and waste counterparts of POs. In general, more liquid and less solid products were obtained from the pyrolysis of fresh plastics compared to plastic wastes. The volatile content of waste plastics is generally lower than that of fresh plastics (Jung et al. 2010; Mastellone et al. 2002; Phyllis2 2022), which explains the difference between the liquid yields of these two. Also, the additives, colorants, and stabilizers, which generally consist of inorganic substances, increase the ash content in the waste plastics, which is associated with an increased solid product (Gala, Guerrero, and Serra 2020). There were no significant changes in gas yield as the optimum conditions were applied to maximize the liquid yield. The lowest overall conversion efficiency and lower yields were obtained for HDPE due to its linear chain of hydrocarbons leading to the higher activation energy for bond breaking (Chowlu, Reddy, and Ghoshal 2009; Dubdub and Al-Yaari 2020; Frączak, Fabiś, and Orlińska 2021). Although the experiments on LDPE with branched hydrocarbon chains resulted in higher liquid yield, complete conversions were not achieved. PP is the only PO type that has complete conversion efficiency. On the other hand, the F-Mix experiment has the highest liquid yield. A blend consisting mainly of PP can compensate for the disadvantages of HDPE and LDPE, allowing higher conversion efficiencies and liquid yields.

The properties of the liquid products are listed in Table 5.1. Pyrolysis of POs was carried out at 450 °C, with the main product typically being the waxy products (C_{21+} hydrocarbons) (R. Aguado et al. 2002; M. Arabiourrutia et al. 2012). Contrary to the general trend for pyrolysis of POs at 450 °C, lighter hydrocarbons (C_5-C_{20} hydrocarbons) were favored, and the wax yield of POs was not higher than 12% in this study. Although suppression of vapor residence time was targeted by increasing the N_2 flow rate, the use of a higher feeding rate (1.5 g/min) reduced the vapor movement in the reactor, maximizing wax cracking during pyrolysis. This trend was also observed in the work of Mastral *et al*. (José F. Mastral, Berrueco, and Ceamanos 2006), where a laboratory- scale pyrolysis system under conditions similar to the conditions used in the Set-1 was

operated. The liquid composition exists in the experiments that used mainly the PP as feedstock (*i.e.,* F-PP, W-PP, F-Mix, and W-Mix), gasoline-range hydrocarbons (C_5-C_{12}), while diesel-range hydrocarbon production was favored in the experiments using F-LDPE, F-HDPE, W-LDPE, and W-HDPE. The activation energy for bond breaking is in ascending order PP < LDPE < HDPE (Chowlu, Reddy, and Ghoshal 2009; Dubdub and Al-Yaari 2020). For this reason, the production of heavier hydrocarbons is favored in LDPE and HDPE and vice versa in PP. On the other hand, many studies using PP (Murata et al. 2002; Murata, Brebu, and Sakata 2009a, 2010), (Auxilio et al. 2017; Murata, Brebu, and Sakata 2010) and LDPE (M. Arabiourrutia et al. 2012; Serrano et al. 2001) as feedstocks for pyrolysis have found a similar trend. It should be noted that to overcome heat transfer limitations, reactors (*e.g.,* CSBRs, CSTRs) and/or thermal pretreatment units (*e.g.,* extruders) were used in the majority of these studies. In our case, due to the high feed rate, a pool of hot molten plastic was created to overcome this drawback. The similarity between our results and those in the literature proves that our intention was successful. The HHV of liquid products varied between 50 and 52 MJ/kg. Although the HHVs of liquids have great energy potential, these results are not in line with the findings reported in the literature (*i.e.,* 40 to 50 MJ/kg) (Elordi et al. 2011; Kunwar, Moser, et al. 2016; Jin et al. 2018). As mentioned in Figure 5.3, unsaturated hydrocarbon production was favored by all feedstocks that elevated the hydrogen to carbon (H/C) ratio which can be the reason for the higher HHVs determined (Yildiz, Ronsse, and Prins 2017). The atomic carbon numbers in the liquid yields of pyrolysis of F-PP and W-PP experiments ranged from C_9 to C_{11}, as shown in Figure 5.2. The atomic carbon numbers for F-LDPE, F-HDPE, W-LDPE and W-HDPE showed a more uniform carbon distribution up to C_{18} compared to the experiments of PP. In the polyethylene experiments, most of the carbon atoms were found to be at C_{18+}, where the paraffins are mainly present. This can be explained by the stability of PEs favoring the intermolecular hydrogen transfer reactions (Jin et al. 2018). The carbon distribution of F-Mix and W-Mix is quite similar to that of the plastics that make up the mixture. The PE content decreases the yield of lighter hydrocarbons, while in the presence of PE more C_{13+} hydrocarbons are produced than in individual PP experiments.
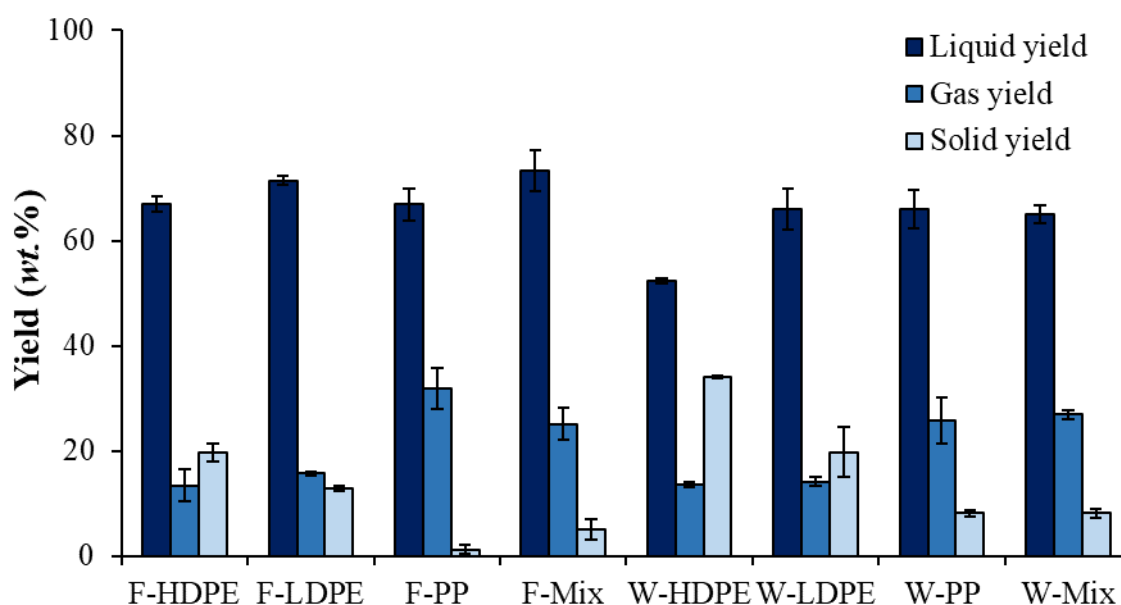
Figure 5.1. The mass balances of experiments involving the pyrolysis of POs.

Figure 5.3 shows the composition of liquids obtained by the Set-1 experiments. The F-PP and W-PP experiments resulted mainly in naphtenes, followed by olefins. For the LDPE and HDPE experiments, the main major products are paraffins and olefins, which have almost the same percentage and contain very small amounts of naphtenes compared to the PP experiments. Since the ratio of PP to PE in the mixtures is 1:1, the liquid composition in terms of bonding type is as in the PP and PE experiments. The content of diolefins, cyclic olefins and aromatics can be considered in trace amounts for all experiments. The ratio of the yields of unsaturated hydrocarbons (*i.e.,* olefins, cycloalkenes, and diolefins) to paraffins and isoparaffins (*i.e.,* saturated hydrocarbons) should be considered to understand the majority of primary and secondary reactions (Abbas-Abadi et al. 2022). In this study, the aforementioned ratio is less than 19, 2, 1.5 and 4.5 for fresh and waste PP, LDPE, HDPE and the blends, respectively. In contrast to other experiments, secondary reactions occurred predominantly in the pyrolysis of PP. This is the reason why in the experiments of PP almost complete conversion of hydrocarbons from the gasoline range is achieved. However, no aromatization reactions occurred for F-PP and W-PP. To produce oil with similar quality to commercial oils, increasing the temperature (M. Arabiourrutia et al. 2012) or using a catalyst that favors aromatics through Diels-Alder reactions (Park, Jeong, and Kim 2019) may be a good solution to increase both the aromatics content in liquids and the energy value of the gas

product through H_2 production. Intermolecular hydrogen transfer (*i.e.,* alkane production) and condensation reactions (*i.e.,* naphthene production) are more dominant than β-cleavage (*i.e.,* olefin production) in F-Mix and W-Mix (Jin et al. 2018), but the experiments still resulted in a high ratio of unsaturated to saturated hydrocarbons. The studies reported that increasing the PE ratio in the POs mixture leads to higher yield of paraffins (Frączak, Fabiś, and Orlińska 2021; Predel and Kaminsky 2000; Jin et al. 2018). Increasing the HDPE and LDPE content in the blend can prevent excessive cracking during pyrolysis.

The compositions and the energy recovery of the gases for bond breaking for the experiments in Set-1 are listed in Table 5.2. In all experiments, C_3 hydrocarbons, especially propylene, are the main products in the gases. The C_3 hydrocarbons are followed by C_2 gases, while the methane yield is the lowest. No hydrogen was produced in the experiments in this set. The production of propylene at mild temperatures and under high inert gas flow rates is common in the non-catalytic pyrolysis of POs (Elordi et al. 2011; Park et al. 2018; Predel and Kaminsky 2000; Serrano et al. 2001). The thermal stability of lighter NCGs (*e.g.,* methane, hydrogen) is low under the process conditions. Therefore, hydrogen production is not triggered even in the F-PP and W-PP experiments where the secondary reactions were enhanced because the process conditions (*i.e.,* feed intake, N_2 flow rate) could not provide sufficient energy for hydrogen production. The studies reported that hydrogen production was enhanced at a temperature above 600 ℃ by dehydrogenation reactions after aromatization reactions (Jung et al. 2010; J. F. Mastral et al. 2006), while propylene production decreased.

Table 5.1. Liquid product characteristics of individual and mixed POs (Temperature is 450 °C; N_2 flow rate is 1.1 L/min.).

Sample	Mixing ratio (wt.%)	Liquid yield (*wt.%*)	Composition of liquid products (yields, %)			HHV (MJ/kg)
	HDPE: LDPE: PP		C_5-C_{12} hydrocarbons	C_{13}-C_{20} hydrocarbons	C_{21+} hydrocarbons	
F-HDPE	100:0:0	41.2	22.7	69.8	7.74	52.3
F-LDPE	0:100:0	66.0	24.7	58.3	4.48	52.8
F-PP	0:0:100	66.0	98.9	1.07	0.00	50.9
F-Mix	25:25:50	65.0	66.0	30.6	6.20	51.8
W-HDPE	100:0:0	67.0	24.1	67.8	7.36	51.2
W-LDPE	0:100:0	71.5	27.2	57.0	11.6	52.7
W-PP	0:0:100	66.9	94.9	5.15	0.00	51.5
W-Mix	25:25:50	73.3	57.5	33.9	5.22	52.0

All experiments in Set-1 were sufficient to provide energy for endothermic bond breaking during pyrolysis. Since the gas yields of the experiments varied from 13 wt.% to 31 wt.%, the calculated energies of the NCGs exceeded the energy requirement of one experiment. Since the gas yields were higher for pure plastics due to higher volatiles and a lack of inorganic additives, the calculated energy recovery for pyrolysis of pure plastics is higher than for the experiments with waste plastics, except for the experiments with mixed plastics (*i.e.,* F-Mix and W-Mix). The volatile content of individual fresh plastics could not be converted into condensable gases and NCGs during pyrolysis due to the short process duration. The conversion efficiency for individual waste plastics was considerably high depending on how many times plastics are treated mechanically (*i.e.,* aging) (Abbas-Abadi et al. 2022). In addition to the aging factor, the positive synergistic effect between POs during pyrolysis increased the gas yield, resulting in NCGs from W-Mix having higher energy than F-Mix.
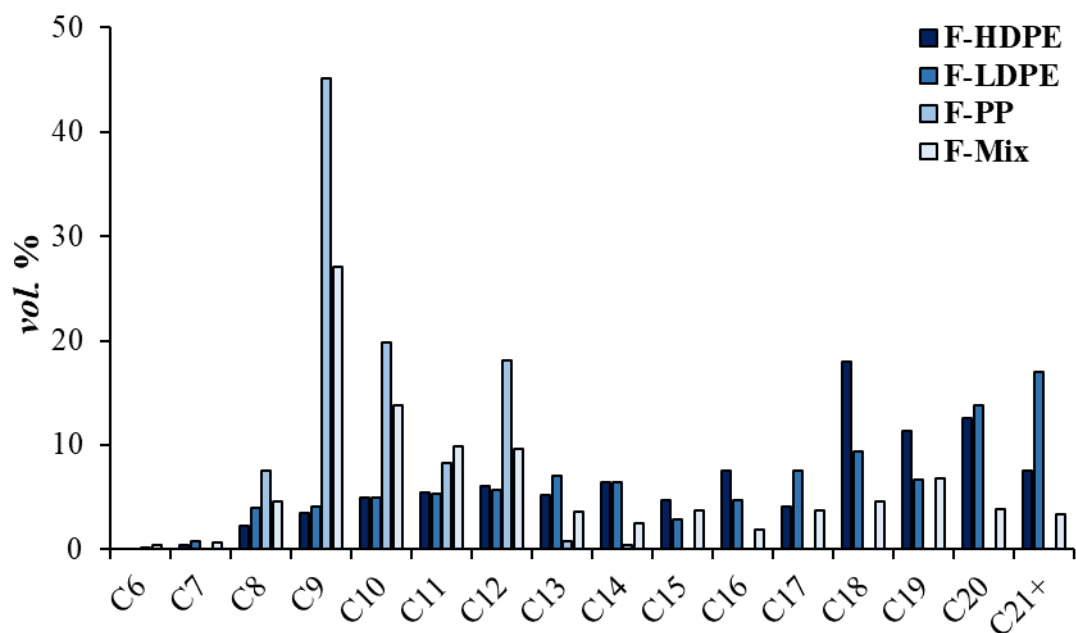
(a)
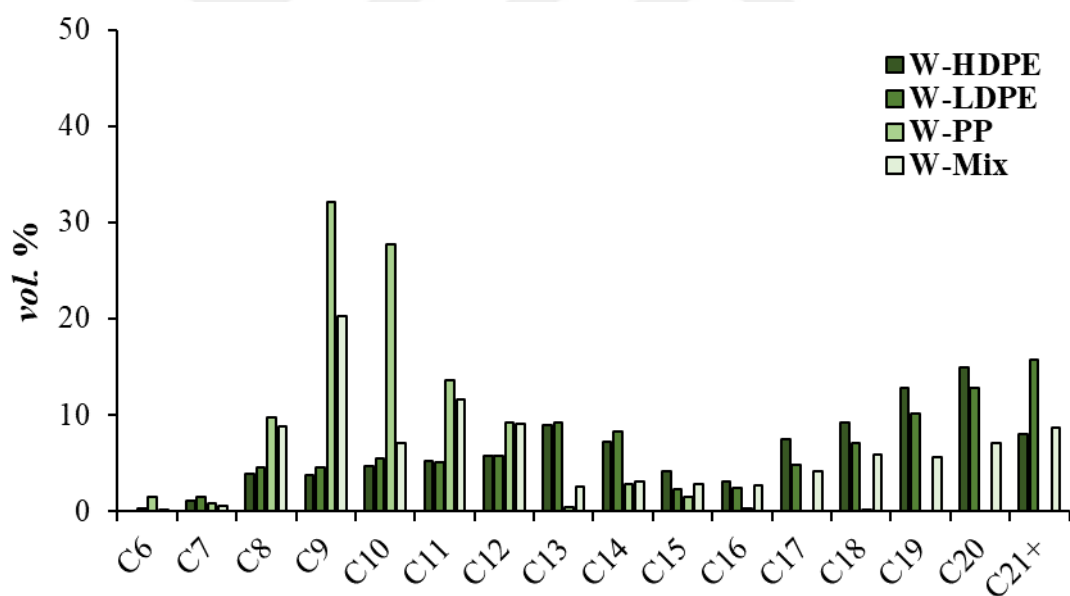
(b)

Figure 5.2. Carbon atom numbers of pyrolysis of a) fresh plastics, b) waste plastics (Temperature is 450 ℃; N_2 flow rate is 1.1 L/min.).
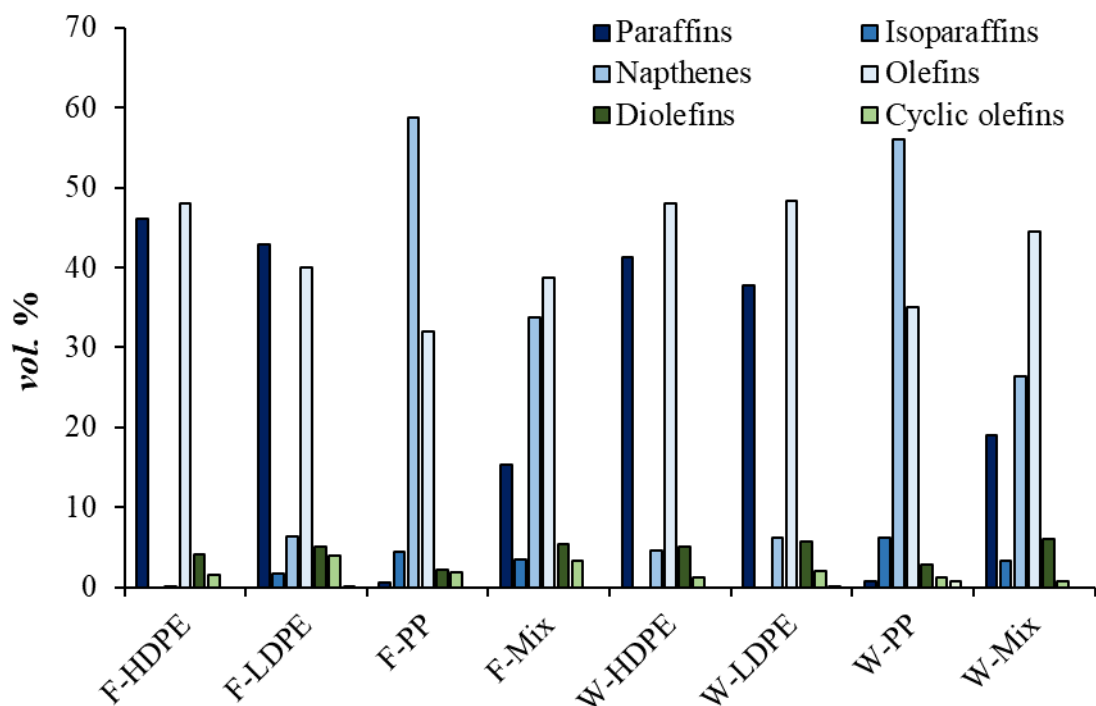
Figure 5.3. The composition of liquid products of the experiments in the Set-1
(Temperature is 450 °C; N2 flow rate is 1.1 L/min.).

Table 5.2. Gas composition and their energy recovery of the experiments in the Set-1
(Temperature is 450 °C; N_2 flow rate is 1.1 L/min.).

	CH_4 (wt.%)	C_2H_4 (wt.%)	C_2H_6 (wt.%)	C_3H_6 (wt.%)	C_3H_8 (wt.%)	Energy values of NCG (kJ)*	% energy provided by NCG required by the pyrolysis process*
F-HDPE	4.88	16.7	14.0	42.8	21.5	603	239
F-LDPE	6.87	15.2	21.2	45.1	11.7	800	281
F-PP	3.05	4.10	10.4	77.0	5.42	1420	564
F-Mix	3.63	6.06	12.1	64.8	13.4	967	384
W-HDPE	3.66	10.2	12.7	48.4	25.0	612	242
W-LDPE	4.91	14.7	15.2	40.0	25.4	641	254
W-PP	3.15	5.03	9.48	74.1	8.21	1150	458
W-Mix	4.23	8.89	13.1	72.1	1.64	1203	478

* Calculated by Equation 1.1 and Equation 1.2

5.3.   Conclusions

The higher yields of the liquid product were recovered from fresh POs compared to waste POs in Set-1 due to a higher volatile content and lack of additives such as minerals as colorants. F-PP and WPP were almost completely converted to gasoline range hydrocarbons, while heavier fuels, mainly C_{13}-C_{20} hydrocarbons, were produced from HDPE and LDPE. Mixing PEs with PP had a positive effect on the activation energy for bond breaking, resulting in more liquid products compared to individual PE experiments. The production of unsaturated hydrocarbons, indicative of secondary reactions in liquids, decreased with F-Mix and W-Mix compared to F-PP and W-PP. The yield of aromatics was 0.11 vol%, 0.16 vol% and 0.82 vol% for F-LDPE, W-LDPE and W-PP, respectively. No aromatization reaction took place for the other feedstocks.

The gas yields were higher for fresh plastics than for waste plastics. The only exception was the pyrolysis of W-Mix. Gas formation accelerated due to the positive synergistic effect of the POs and the weak binding of the waste plastics. The NCGs consisted mainly of propylene, which is thermally stable at 450 °C, while no H_2 production was observed for the Set-1 due to the lack of dehydrogenation reactions. The calculated energy of the NCGs was sufficient to provide the energy for the endothermic bond breaking of the POs in all experiments of Set-1. The experiments show that pyrolysis of POs, regardless of their state (*i.e.,* fresh or waste), is an energetically sufficient process with respect to bond breaking. The results show that NCGs of non-catalytic pyrolysis have great potential to provide energy not only for bond breaking but for the other unit operations (*e.g.,* heating the reactor, and condensation system). Given these data, non-catalytic and continuous pyrolysis of PO waste can provide energy self-sustaining pyrolysis while solving the problem of alternative fuel production and non-recycled waste. Since the approach does not require a sophisticated waste separation system and is operated under mild conditions, the study can provide an economical way to produce liquids and gas fuels.

CHAPTER 6

CATALYTIC PYROLYSIS OF WASTE POLYOLEFINS

6.1. Introduction

Catalysts allows to study at a lower temperature (Borsella et al. 2018), provides narrower product distribution (Zeaiter 2014) and regulates the aromatic content which is directly related with aromatic content with a tailored acidity (M. Artetxe et al. 2012). Zeolites with a strong acidity are commonly preferred to produce gasoline range hydrocarbon production with a standardized amount of benzene, toluene, and xylene (BTX) content(Norbert Miskolczi, Wu, and Williams 2016; Borsella et al. 2018) thanks to zeolites' shape selectivity. A typical catalytic pyrolysis of POs route based on carbonium theory is represented in Figure 6.1 which is following chain scission, isomerization, oligomerization, hydrogen transfer, and aromatization (Yuan et al. 2022).

Pore size, active surface area, and acidity are the most important factors for zeolites that affect their effectiveness and selectivity. Among the zeolite types, ZSM-5 is the most suitable catalyst to aromatics and NCGs productions thanks to its pore size (*ca.* 5.2 - 5.9 Å) (Yuan et al. 2022) , while Y-zeolites and β-zeolites lead light liquids and intermediate products, respectively (Orozco et al. 2021). In this study, ZSM-5 zeolite whose acidity is 30 was used to enhance aromatization reactions.
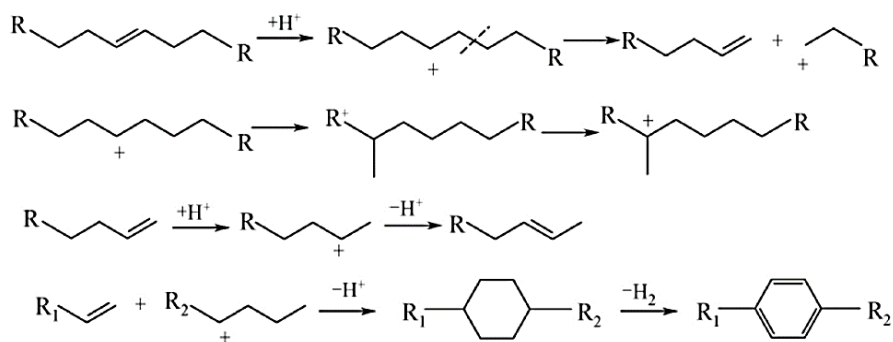

Figure 6.1. Pyrolysis reaction routes of POs in the presence of a solid acid catalyst based on carbonium ion theory [132]

6.2. Results and Discussion

The mass balance and the characteristics of liquid products of experiments in Set-2 are given in Table 6.1. To provide a comparative representation, the non-catalytic experiments of F-Mix and W-Mix are also listed here. The liquid yield decreased with a gradual increase in the C/P ratio, while the gas yield increased. Since the catalysts allow to pyrolyze POs at lower temperatures (Borsella et al. 2018), the elevated gas formation at 450 °C where the non-catalytic experiments took place is expected.

ZSM-5 (*i.e.,* SiO_2/Al_2O_3 ratio of 30) has a great capability of cracking longer chain hydrocarbons (*e.g.* ,C_{21+} hydrocarbons) (Maite Artetxe et al. 2013) so complete conversion of POs mixtures and complete wax cracking were observed for all catalytic experiments as mentioned in Table 6.1. The main fraction in liquid products was gasoline range hydrocarbons for both non-catalytic and catalytic experiments. In the presence of catalyst regardless of C/P ratio, a narrower range of hydrocarbons (*i.e.,* mostly C_7-C_{12}) were produced compared to non-catalytic experiments (see Figure 6.2). The gasoline range hydrocarbons production were enhanced by an increase in the C/P ratio from 1/100 to 1/60 while C_{13}-C_{20} production was limited. A similar trend was observed by Artetxe *et al.*(Maite Artetxe et al. 2012), Seo *et al.* (Seo, Lee, and Shin 2003), Lin and Yen (Lin and Yen 2005) who investigated pyrolysis of POs with C/P ratios with HZSM-5 (*i.e.,* Si/Al =30). HHVs of liquids of catalytic experiments were higher than non-catalytic experiments' liquids. Also, liquid product of W-C100 had the highest HHV but the HHVs of liquids of catalytic experiments were similar. HHVs of liquids of catalytic experiments were higher than the liquids of non-catalytic experiments that can be explained with increase in aromatics yield in liquids in addition to unsaturated hydrocarbons yields. Hydrogen to carbon ratio (H/C) is directly related calorific value of fuels so increase in unsaturated hydrocarbons like cyclic olefins, naphtenes in liquid product in addition to sharp increase in BTX content can explain the increase in HHVs.

Figure 6.3 shows the bond nature of liquid products of non-catalytic and catalytic experiments of mixed POs. The major products are olefins were noncatalytic experiments which gave place to naphtenes and aromatics with gradual increase in C/P ratio. BTX content were 7.61 vol%, 21.4 vol%, and 42.4 vol% for W-C100, W-C80, and W-C60 experiments, respectively. The total aromatic content should be less than 35 vol %, while

the maximum allowable benzene yield is set to 1 vol% by European Union regulations (Concawe 2002). Although the aromatics yield is in the range of the regulations for W-C100 and W-C80 experiments, the benzene yields were 2.1 vol% and 8.5 vol% for W-C100 and W-C80, respectively. It shows that C/P ratios used in this study were higher than the required amount. Using a lower C/P ratio enhances the quantity and quality of liquids according to the regulations. Another solution for exceeding the limits can be usage of a ZSM-5 with less acidity (*e.g.,* 50 and 280) (Maite Artetxe et al. 2013) or regulating catalyst's acidity with metals (e.g Ni and Ga) (Yuan et al. 2022).
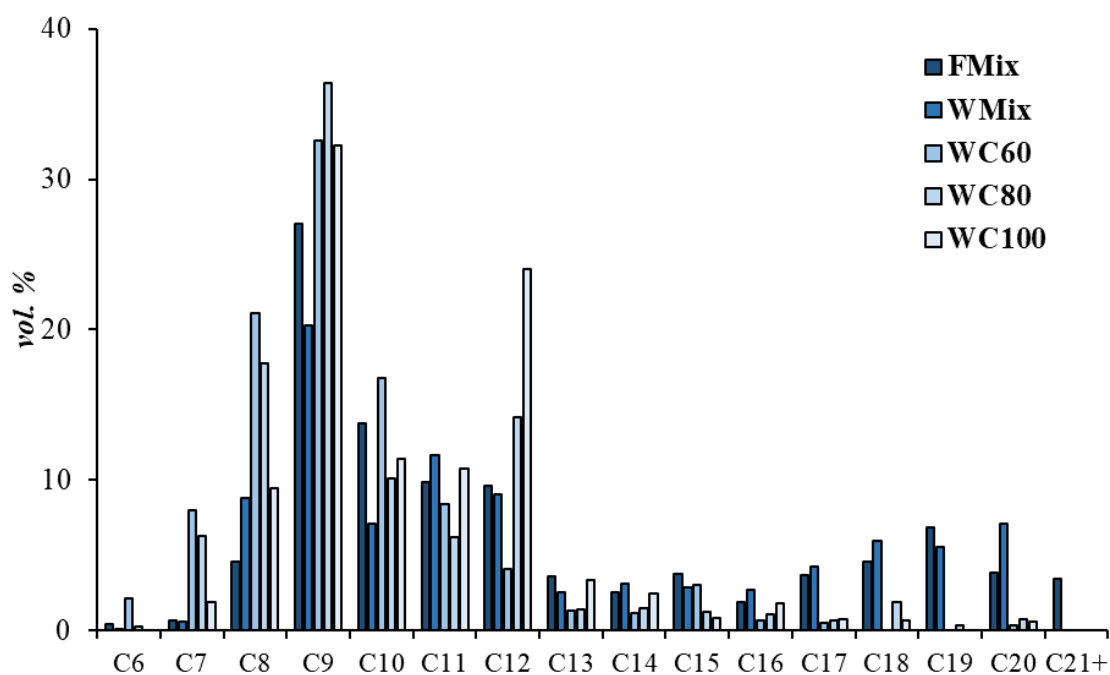
Figure 6.2. Carbon atom numbers of pyrolysis of non-catalytic and catalytic experiments (Temperature is 450 °C; N_2 flow rate is 1.1 L/min.).

Table 6.1. Liquid product characteristics of individual and mixed POs (Temperature is 450 °C; N_2 flow rate is 1.1 L/min.).

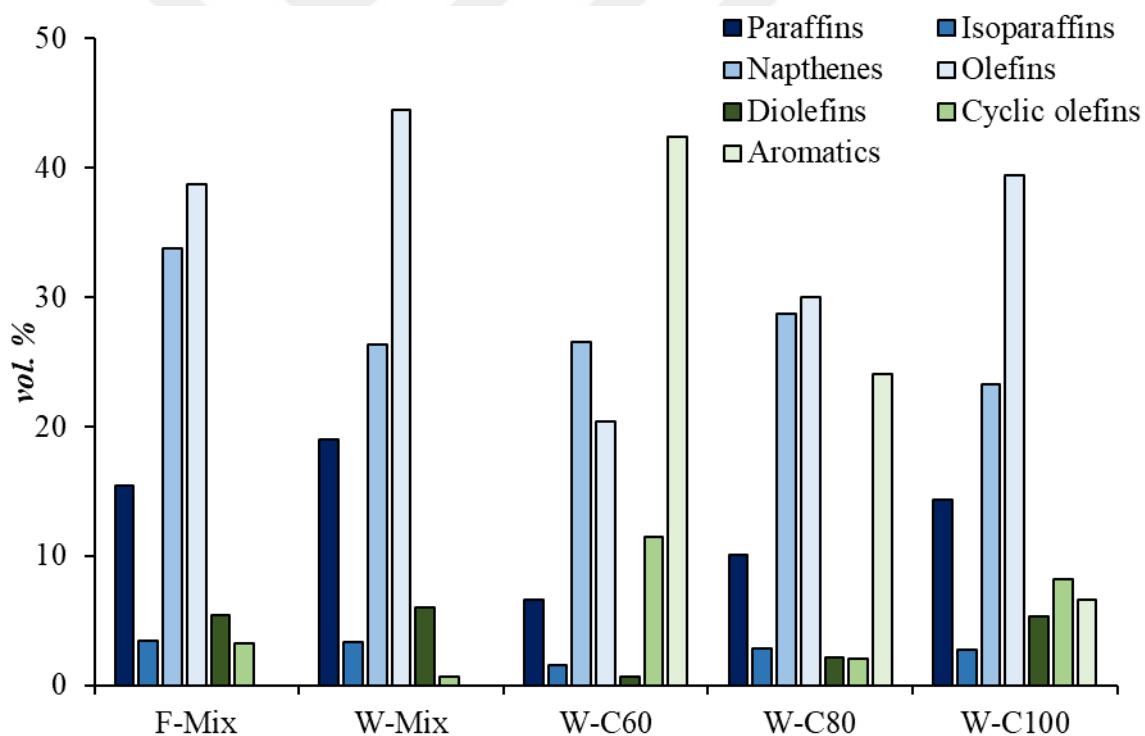| Sample	Mixing ratio (wt.%)	Liquid yield (wt.%)	Liquid product characteristics (yield, vol.%)			HHV (MJ/kg)	Gas yield (wt.%)	Solid yield (wt.%)
	HDPE: LDPE: PP		C_5-C_{12} HCs	C_{13}-C_{20} HCs	C_{21+} HCs			
F-Mix	25:25:50	73.3	66.0	30.6	6.20	51.8	26.9	2.22
W-Mix	25:25:50	65.0	57.5	33.9	5.22	52.0	26.9	8.05
W-C60	25:25:50	30.9	93.0	7.00	0.00	53.7	64.1	5.00
W-C80	25:25:50	36.8	91.2	8.85	0.00	52.6	61.2	2.03
W-C100	25:25:50	51.8	89.7	10.37	0.00	53.9	41.6	5.08

Figure 6.3. The bond nature of noncatalytic and catalytic experiments (Temperature is 450 °C; N_2 flow rate is 1.1 L/min.).

76

6.3. Conclusions

In this part, the catalytic pyrolysis of mixed POs was studied. The optimum conditions discussed in section 4.3 were chosen as pyrolysis conditions. The results of the catalytic experiments were compared with non-catalytic experiments performed under the same conditions. As the C/P ratio increased, the liquid yield decreased while the gas formation accelerated due to excessive cracking. All waxy products (C_{21+} hydrocarbons) present in the non-catalytic experiments were converted to lighter hydrocarbons in the presence of the ZSM-5 catalyst, regardless of the C/P ratio. The liquid products of the experiments consisted mostly of hydrocarbons in the gasoline range, especially in the C_7-C_{12} range.

Thanks to the high aromatics content and the high H/C ratio, the HHV of the liquids varied between 52.6 and 53.9 MJ/kg. The liquid products of the W-C80 and W-C100 experiments had a total aromatics content of less than 35 vol%, but the benzene content (*i.e.,* 8.5 vol.% for W-C80, 2.1 vol.% for W-C100) was too high for both experiments according to the regulations. The fluid quality of the W-C60 experiment was not within the range of the regulations. All results show that using a low C/P ratio and/or adjusting the acidity of ZSM-5 can help to achieve a high liquid yield with higher quality.

CONCLUSIONS

This study consists of a critical literature review (CHAPTER 3), optimization of pyrolysis conditions for maximizing POs by Taguchi's orthogonal array (CHAPTER 4), characterization of fresh and waste POs' liquids and utilizing tail gases as an energy source for pyrolysis (CHAPTER 5), and catalytic pyrolysis of waste mix POs (CHAPTER 6). The main conclusions are listed below:

- CSTRs are found to be the best-performing reactors for both liquid and gasoline production at lower temperatures (*ca.* 420 °C) compared to the operating temperatures CSBRs and BFBRs for pyrolysis of HDPE in the literature part.

- At a temperature higher than 550 °C, the yield of the liquid product decreases for pyrolysis of PP in the literature part.

- The data obtained from the literature shows that 90 wt.% of liquid production and suppressing wax formation are possible at temperatures below 450 °C if the heat transfer limitations are eliminated by using a proper reactor, heat carrier and/or pretreatment reactor.

- 0.9 L/min as N_2 flow rate, 15 min feeding period, 30 g as a plastic amount per feeding, and 0 °C as condensation temperature were the predicted optimal pyrolysis conditions for LDPE. At the optimum conditions, 96.7 wt.% of liquid production was calculated.

- The maximum liquid yield (*ca.* 78.4 wt.%) can be obtained at an N_2 flow rate of 1.00 L/min, a feeding time of 20 min, a plastic amount of 20 g per feeding, and a condenser temperature of 0 °C for the pyrolysis of PP.

- The optimal conditions for the experimental series are 1.1 L/min as the N_2 flow rate, 1.5 g/min for feed intake, and Mix-3 (25:25:50; HDPE: LDPE: PP) as the mixing ratio. 74.1 wt.% liquid yield was predicted while confirmatory experiments yielded 73.3 wt.% liquid.

- The higher yields of the liquid product were recovered from fresh POs compared to waste POs.

- The production of unsaturated hydrocarbons, indicative of secondary reactions in liquids, decreased with fresh and waste plastic mixture (F-Mix and W-Mix) compared to F-PP and W-PP.

- The yield of aromatics was 0.11 *vol.*%, 0.16 *vol.*% and 0.82 *vol.*% for F-LDPE, W-LDPE, and W-PP, respectively.

- The gas yields were higher for fresh plastics than for waste plastics.

- The NCGs consisted mainly of propylene.

- The calculated energy of the NCG was sufficient to provide the energy for the endothermic bond breaking of the POs in all experiments in Set-1.

- As the C/P ratio increased, the liquid yield decreased while the gas formation accelerated due to secondary reactions.

- The liquid products of the experiments in Set-2 are composed of mostly hydrocarbons in the gasoline range.

- The highest aromatic content, 42.4 vol.%, was achieved by the W-C60 experiment (*i.e.,* the highest C/P ratio).

APPENDIX A

PUBLICATIONS RELATED TO THIS THESIS

1.   Ekici, E., Yildiz, G., Analysis of Pyrolysis Process Parameters for the Maximized Production of Gasoline-range Renewable Fuels from High-density Polyethylene, International Symposium on Energy Management and Sustainability (ISEMAS) 2022, 2022, Virtual Event

2.   Ekici, E., Yildiz, G., Determination of optimal pyrolysis process parameters to maximize gasoline-like renewable fuel production from polypropylene, XI The International Scientific Conference Innovations-Sustainability-Modernity-Openness (ISMO), 2022, Bialystok, Poland.

3.   Ekici, E., Yildiz, G. Analysis of process parameters and assessing the possibility of utilizing the tail gases as energy sources for the pyrolysis of polyolefins, 9th International Conference on Sustainable Solid Waste Management (CORFU2022), 2022, Corfu, Greece.

4.   Ekici, E., Yildiz G., Joka-Yildiz, M., Wang, J., Analysis of process parameters and assessment of tail gases as energy sources for the pyrolysis of polyolefins, Energy 2022. (Under preparation)

5.   Cheng, Y., Ekici, E., Yildiz, G., Yang, Y., Coward, B., Wang, J., Applied machine learning for prediction of waste plastic pyrolysis towards valuable fuel and chemicals production, Journal of Analytical and Applied Pyrolysis 2022. (Accepted).

REFERENCES

Abbas-Abadi, Mehrdad Seifali, Mehdi Nekoomanesh Haghighi, and Hamid Yeganeh. 2012. "Effect of the Melt Flow Index and Melt Flow Rate on the Thermal Degradation Kinetics of Commercial Polyolefins." *Journal of Applied Polymer Science* 126 (5): 1739–45. https://doi.org/10.1002/app.36775.

Abbas-Abadi, Mehrdad Seifali, Azd Zayoud, Marvin Kusenberg, Martijn Roosen, Florence Vermeire, Parviz Yazdani, Jonathan Van Waeyenberg, et al. 2022. "Thermochemical Recycling of End-of-Life and Virgin HDPE: A Pilot-Scale Study." *Journal of Analytical and Applied Pyrolysis* 166 (July). https://doi.org/10.1016/j.jaap.2022.105614.

Abdy, Charlotte, Yuqing Zhang, Jiawei Wang, Yang Yang, Ignacio Artamendi, and Bob Allen. 2022. "Pyrolysis of Polyolefin Plastic Waste and Potential Applications in Asphalt Road Construction: A Technical Review." *Resources, Conservation and Recycling* 180 (January): 106213. https://doi.org/10.1016/j.resconrec.2022.106213.

Aboulkas, A, K El, and A El Bouadili. 2010. "Thermal Degradation Behaviors of Polyethylene and Polypropylene . Part I : Pyrolysis Kinetics and Mechanisms." *Energy Conversion and Management* 51 (7): 1363–69. https://doi.org/10.1016/j.enconman.2009.12.017.

Aguado, J., D. P. Serrano, J. M. Escola, and E. Garagorri. 2002. "Catalytic Conversion of Low-Density Polyethylene Using a Continuous Screw Kiln Reactor." *Catalysis Today* 75 (1–4): 257–62. https://doi.org/10.1016/S0920-5861(02)00077-9.

Aguado, Roberto, Martín Olazar, María J. San José, Beatriz Gaisán, and Javier Bilbao. 2002. "Wax Formation in the Pyrolysis of Polyolefins in a Conical Spouted Bed Reactor." *Energy and Fuels* 16 (6): 1429–37. https://doi.org/10.1021/ef020043w.

Al-Salem, Sultan M. 2018. *Feedstock and Optimal Operation for Plastics to Fuel Conversion in Pyrolysis*. *Plastics to Energy: Fuel, Chemicals, and Sustainability Implications*. Elsevier Inc. https://doi.org/10.1016/B978-0-12-813140-4.00005-4.

Al-Salem, Sultan Majed, and Animesh Dutta. 2021. "Wax Recovery from the Pyrolysis of Virgin and Waste Plastics." *Industrial and Engineering Chemistry Research* 60 (22): 8301–9. https://doi.org/10.1021/acs.iecr.1c01176.

Al-Salem, Sultan Majed, Yang Yang, Jiawei Wang, and Gary Anthony Leeke. 2020.

"Pyro-Oil and Wax Recovery from Reclaimed Plastic Waste in a Continuous
Auger Pyrolysis Reactor." *Energies* 13 (8). https://doi.org/10.3390/en13082040.

Alavi-Borazjani, Seyedeh Azadeh, Luís António da Cruz Tarelho, and Maria Isabel
Capela. 2021. "Parametric Optimization of the Dark Fermentation Process for
Enhanced Biohydrogen Production from the Organic Fraction of Municipal Solid
Waste Using Taguchi Method." *International Journal of Hydrogen Energy* 46
(41): 21372–82. https://doi.org/10.1016/j.ijhydene.2021.04.017.

Anene, Azubuike Francis, Siw Bodil Fredriksen, Kai Arne Sætre, and Lars Andre
Tokheim. 2018. "Experimental Study of Thermal and Catalytic Pyrolysis of Plastic
Waste Components." *Sustainability (Switzerland)* 10 (11): 1–11.
https://doi.org/10.3390/su10113979.

Anuar Sharuddin, Shafferina Dayana, Faisal Abnisa, Wan Mohd Ashri Wan Daud, and
Mohamed Kheireddine Aroua. 2016. "A Review on Pyrolysis of Plastic Wastes."
Energy Conversion and Management 115: 308–26.
https://doi.org/10.1016/j.enconman.2016.02.037.

Arabiourrutia, M., G. Elordi, G. Lopez, E. Borsella, J. Bilbao, and M. Olazar. 2012.
"Characterization of the Waxes Obtained by the Pyrolysis of Polyolefin Plastics in
a Conical Spouted Bed Reactor." *Journal of Analytical and Applied Pyrolysis* 94:
230–37. https://doi.org/10.1016/j.jaap.2011.12.012.

Arabiourrutia, Miriam, Gorka Elordi, Martin Olazar, and Javier Bilbao. 2017.
"Pyrolysis of Polyolefins in a Conical Spouted Bed Reactor: A Way to Obtain
Valuable Products." In *Pyrolysis*. Vol. 2014. https://doi.org/10.5772/67706.

Armenise, Sabino, Wong SyieLuing, José M. Ramírez-Velásquez, Franck Launay,
Daniel Wuebben, Norzita Ngadi, Joaquín Rams, and Marta Muñoz. 2021. "Plastic
Waste Recycling via Pyrolysis: A Bibliometric Survey and Literature Review."
Journal of Analytical and Applied Pyrolysis 158.
https://doi.org/10.1016/j.jaap.2021.105265.

Artetxe, M., G. Lopez, M. Amutio, G. Elordi, J. Bilbao, and M. Olazar. 2012. "Light
Olefins from HDPE Cracking in a Two-Step Thermal and Catalytic Process."
Chemical Engineering Journal 207–208: 27–34.
https://doi.org/10.1016/j.cej.2012.06.105.

Artetxe, Maite, Gartzen Lopez, Maider Amutio, Itsaso Barbarias, Aitor Arregi, Roberto
Aguado, Javier Bilbao, and Martin Olazar. 2015. "Styrene Recovery from
Polystyrene by Flash Pyrolysis in a Conical Spouted Bed Reactor." *Waste*

Management 45: 126–33. https://doi.org/10.1016/j.wasman.2015.05.034.

Artetxe, Maite, Gartzen Lopez, Maider Amutio, Gorka Elordi, Javier Bilbao, and Martin Olazar. 2013. "Cracking of High Density Polyethylene Pyrolysis Waxes on HZSM-5 Catalysts of Different Acidity." *Industrial and Engineering Chemistry Research* 52 (31): 10637–45. https://doi.org/10.1021/ie4014869.

Artetxe, Maite, Gartzen Lopez, Maider Amutio, Gorka Elordi, Martin Olazar, and Javier Bilbao. 2010. "Operating Conditions for the Pyrolysis of Poly-(Ethylene Terephthalate) in a Conical Spouted-Bed Reactor." *Industrial and Engineering Chemistry Research* 49 (5): 2064–69. https://doi.org/10.1021/ie900557c.

Artetxe, Maite, Gartzen Lopez, Gorka Elordi, Maider Amutio, Javier Bilbao, and Martin Olazar. 2012. "Production of Light Olefins from Polyethylene in a Two-Step Process: Pyrolysis in a Conical Spouted Bed and Downstream High-Temperature Thermal Cracking." *Industrial and Engineering Chemistry Research* 51 (43): 13915–23. https://doi.org/10.1021/ie300178e.

ASTM International. n.d. "ASTM D7611/D7611M-21." *2022*.

Auxilio, Anthony R., Wei Lit Choo, Isha Kohli, Srikanth Chakravartula Srivatsa, and Sankar Bhattacharya. 2017. "An Experimental Study on Thermo-Catalytic Pyrolysis of Plastic Waste Using a Continuous Pyrolyser." *Waste Management* 67: 143–54. https://doi.org/10.1016/j.wasman.2017.05.011.

Berrueco, Cesarb, E. J. Mastral, E. Esperanza, and J. Ceamanos. 2002. "Production of Waxes and Tars from the Continuous Pyrolysis of High Density Polyethylene. Influence of Operation Variables." *Energy and Fuels* 16 (5): 1148–53. https://doi.org/10.1021/ef020008p.

Borsella, E., R. Aguado, A. De Stefanis, and M. Olazar. 2018. "Comparison of Catalytic Performance of an Iron-Alumina Pillared Montmorillonite and HZSM-5 Zeolite on a Spouted Bed Reactor." *Journal of Analytical and Applied Pyrolysis* 130 (December 2017): 249–55. https://doi.org/10.1016/j.jaap.2017.12.015.

Borsodi, Nikolett, Norbert Miskolczi, András Angyal, and László Bartha. 2011. "Hydrocarbons Obtained by Pyrolysis of Contaminated Waste Plastics." *45th International Petroleum Conference, Bratislava, Sovak REpublic*, no. 1: 1–9.

Bridgwater, A. V. 1996. "Production of High Grade Fuels and Chemicals from Catalytic Pyrolysis of Biomass." *Catalysis Today* 29 (1–4): 285–95. https://doi.org/10.1016/0920-5861(95)00294-4.

Chandrasekaran, Sriraam R., Bidhya Kunwar, Bryan R. Moser, Nandakishore

Rajagopalan, and Brajendra K. Sharma. 2015. "Catalytic Thermal Cracking of Postconsumer Waste Plastics to Fuels. 1. Kinetics and Optimization." *Energy and Fuels* 29 (9): 6068–77. https://doi.org/10.1021/acs.energyfuels.5b01083.

chemeurope.com. 2022. "Heat of Combustion." 2022. https://www.chemeurope.com/en/encyclopedia/Heat_of_combustion.html.

Chen, Guan Lin, Guan Bang Chen, Yueh Heng Li, and Wen Teng Wu. 2014. "A Study of Thermal Pyrolysis for Castor Meal Using the Taguchi Method." *Energy* 71: 62–70. https://doi.org/10.1016/j.energy.2014.04.009.

Cho, Min Hwan, Su Hwa Jung, and Joo Sik Kim. 2010. "Pyrolysis of Mixed Plastic Wastes for the Recovery of Benzene, Toluene, and Xylene (BTX) Aromatics in a Fluidized Bed and Chlorine Removal by Applying Various Additives." *Energy and Fuels* 24 (2): 1389–95. https://doi.org/10.1021/ef901127v.

Chowlu, Aie Cheng King, P. Karthik Reddy, and A. K. Ghoshal. 2009. "Pyrolytic Decomposition and Model-Free Kinetics Analysis of Mixture of Polypropylene (PP) and Low-Density Polyethylene (LDPE)." *Thermochimica Acta* 485 (1–2): 20–25. https://doi.org/10.1016/j.tca.2008.12.004.

Concawe, Recent. 2002. "The Focus on Aromatics in Automotive Fuels Specifications." *CONCAWE Review* 11 (2): 10–13.

Czajczyńska, D., L. Anguilano, H. Ghazal, R. Krzyżyńska, A. J. Reynolds, N. Spencer, and H. Jouhara. 2017. "Potential of Pyrolysis Processes in the Waste Management Sector." *Thermal Science and Engineering Progress* 3: 171–97. https://doi.org/10.1016/j.tsep.2017.06.003.

Dai, Leilei, Nan Zhou, Yuancai Lv, Yanling Cheng, Yunpu Wang, Yuhuan Liu, Kirk Cobb, Paul Chen, Hanwu Lei, and Roger Ruan. 2022. "Pyrolysis Technology for Plastic Waste Recycling : A State-of-the-Art Review." *Progress in Energy and Combustion Science* 93 (August): 101021. https://doi.org/10.1016/j.pecs.2022.101021.

Davidson, Matthew G., Rebecca A. Furlong, and Marcelle C. McManus. 2021. "Developments in the Life Cycle Assessment of Chemical Recycling of Plastic Waste – A Review." *Journal of Cleaner Production* 293: 126163. https://doi.org/10.1016/j.jclepro.2021.126163.

Dement'ev, Konstantin I., Timur A. Palankoev, Olga A. Alekseeva, Iurii A. Babkin, and Anton L. Maksimov. 2019. "Thermal Depolymerization of Polystyrene in Highly Aromatic Hydrocarbon Medium." *Journal of Analytical and Applied Pyrolysis* 142

(April): 104612. https://doi.org/10.1016/j.jaap.2019.05.001.

Devaraj, J., Y. Robinson, and P. Ganapathi. 2015. "Experimental Investigation of Performance, Emission and Combustion Characteristics of Waste Plastic Pyrolysis Oil Blended with Diethyl Ether Used as Fuel for Diesel Engine." *Energy* 85: 304–9. https://doi.org/10.1016/j.energy.2015.03.075.

Diaz-Silvarrey, Laura S., Andrew McMahon, and Anh N. Phan. 2018. "Benzoic Acid Recovery via Waste Poly(Ethylene Terephthalate) (PET) Catalytic Pyrolysis Using Sulphated Zirconia Catalyst." *Journal of Analytical and Applied Pyrolysis*. https://doi.org/10.1016/j.jaap.2018.08.014.

Diaz Silvarrey, L. S., and A. N. Phan. 2016. "Kinetic Study of Municipal Plastic Waste." *International Journal of Hydrogen Energy* 41 (37): 16352–64. https://doi.org/10.1016/j.ijhydene.2016.05.202.

Dispons, Jean. 2006. "Continuous Thermal Process for Cracking Polyolefin Wastes to Produce Hydrocarbons." In *Feedstock Recycling and Pyrolysis of Waste Plastics: Converting Waste Plastics into Diesel and Other Fuels*, edited by Scheirs John and Walter Kaminsky, 1st ed., 595–604. Wiley. https://doi.org/10.1002/0470021543.

Donaj, Pawel J., W. Kaminsky, F. Buzeto, and W. Yang. 2012. "Pyrolysis of Polyolefins for Increasing the Yield of Monomers' Recovery." *Waste Management* 32 (5): 840–46. https://doi.org/10.1016/j.wasman.2011.10.009.

Dubdub, Ibrahim, and Mohammed Al-Yaari. 2020. "Pyrolysis of Mixed Plastic Waste: I. Kinetic Study." *Materials* 13 (21): 1–15. https://doi.org/10.3390/ma13214912.

Elordi, Gorka, Martin Olazar, Gartzen Lopez, Maite Artetxe, and Javier Bilbao. 2011. "Product Yields and Compositions in the Continuous Pyrolysis of High-Density Polyethylene in a Conical Spouted Bed Reactor." *Industrial and Engineering Chemistry Research* 50 (11): 6650–59. https://doi.org/10.1021/ie200186m.

Fekhar, B., V. Zsinka, and N. Miskolczi. 2019. "Value Added Hydrocarbons Obtained by Pyrolysis of Contaminated Waste Plastics in Horizontal Tubular Reactor: In Situ Upgrading of the Products by Chlorine Capture." *Journal of Cleaner Production* 241: 118166. https://doi.org/10.1016/j.jclepro.2019.118166.

Fivga, Antzela, and Ioanna Dimitriou. 2018. "Pyrolysis of Plastic Waste for Production of Heavy Fuel Substitute: A Techno-Economic Assessment." *Energy* 149: 865–74. https://doi.org/10.1016/j.energy.2018.02.094.

Frączak, Daria, Grażyna Fabiś, and Beata Orlińska. 2021. "Influence of the Feedstock on the Process Parameters, Product Composition and Pilot-Scale Cracking of

Plastics." *Materials* 14 (11): 3094. https://doi.org/10.3390/ma14113094.

Gala, Alberto, Marta Guerrero, and Jose Manuel Serra. 2020. "Characterization of Post-Consumer Plastic Film Waste from Mixed MSW in Spain: A Key Point for the Successful Implementation of Sustainable Plastic Waste Management Strategies." *Waste Management* 111: 22–33. https://doi.org/10.1016/j.wasman.2020.05.019.

Gebre, Shushay Hagos, Marshet Getaye Sendeku, and Mohamed Bahri. 2021. "Recent Trends in the Pyrolysis of Non-Degradable Waste Plastics." *ChemistryOpen* 10 (12): 1202–26. https://doi.org/10.1002/open.202100184.

Goodship, Vannessa. 2007. "Plastic Recycling." *Science Progress* 90 (4): 245–68. https://doi.org/10.3184/003685007X228748.

Ibáñez, M., M. Artetxe, G. Lopez, G. Elordi, J. Bilbao, M. Olazar, and P. Castaño. 2014. "Identification of the Coke Deposited on an HZSM-5 Zeolite Catalyst during the Sequenced Pyrolysis-Cracking of HDPE." *Applied Catalysis B: Environmental* 148–149: 436–45. https://doi.org/10.1016/j.apcatb.2013.11.023.

Jahirul, M I, M G Rasul, D Schaller, M M K Khan, M M Hasan, and M A Hazrat. 2022. "Transport Fuel from Waste Plastics Pyrolysis – A Review on Technologies , Challenges and Opportunities." *Energy Conversion and Management* 258 (February): 115451. https://doi.org/10.1016/j.enconman.2022.115451.

Jeswani, Harish, Christian Krüger, Manfred Russ, Maike Horlacher, Florian Antony, Simon Hann, and Adisa Azapagic. 2021. "Life Cycle Environmental Impacts of Chemical Recycling via Pyrolysis of Mixed Plastic Waste in Comparison with Mechanical Recycling and Energy Recovery." *Science of the Total Environment* 769. https://doi.org/10.1016/j.scitotenv.2020.144483.

Jin, Zechen, Dezhen Chen, Lijie Yin, Yuyan Hu, Huangqing Zhu, and Liu Hong. 2018. "Molten Waste Plastic Pyrolysis in a Vertical Falling Film Reactor and the Influence of Temperature on the Pyrolysis Products." *Chinese Journal of Chemical Engineering* 26 (2): 400–406. https://doi.org/10.1016/j.cjche.2017.08.001.

Jubinville, Dylan, Elnaz Esmizadeh, Sainiwetha Saikrishnan, Costas Tzoganakis, and Tizazu Mekonnen. 2020. "A Comprehensive Review of Global Production and Recycling Methods of Polyolefin (PO) Based Products and Their Post-Recycling Applications." *Sustainable Materials and Technologies* 25: e00188. https://doi.org/10.1016/j.susmat.2020.e00188.

Jung, Su Hwa, Min Hwan Cho, Bo Sung Kang, and Joo Sik Kim. 2010. "Pyrolysis of a Fraction of Waste Polypropylene and Polyethylene for the Recovery of BTX

Aromatics Using a Fluidized Bed Reactor." *Fuel Processing Technology* 91 (3): 277–84. https://doi.org/10.1016/j.fuproc.2009.10.009.

Jung, Su Hwa, Seon Jin Kim, and Joo Sik Kim. 2013. "The Influence of Reaction Parameters on Characteristics of Pyrolysis Oils from Waste High Impact Polystyrene and Acrylonitrile-Butadiene-Styrene Using a Fluidized Bed Reactor." *Fuel Processing Technology* 116: 123–29. https://doi.org/10.1016/j.fuproc.2013.05.004.

Kaminsky, W. 1991. "Recycling of Polymeric Materials by Pyrolysis." *Makromolekulare Chemie. Macromolecular Symposia* 48–49 (1): 381–93. https://doi.org/10.1002/masy.19910480127.

Kang, Bo Sung, Sang Guk Kim, and Joo Sik Kim. 2008. "Thermal Degradation of Poly(Methyl Methacrylate) Polymers: Kinetics and Recovery of Monomers Using a Fluidized Bed Reactor." *Journal of Analytical and Applied Pyrolysis* 81 (1): 7–13. https://doi.org/10.1016/j.jaap.2007.07.001.

Kartik, S., Hemant Kumar Balsora, Manisha Sharma, Agus Saptoro, Rakesh K. Jain, Jyeshtharaj B. Joshi, and Abhishek Sharma. 2022. "Valorization of Plastic Wastes for Production of Fuels and Value-Added Chemicals through Pyrolysis – A Review." *Thermal Science and Engineering Progress* 32: 101316. https://doi.org/10.1016/j.tsep.2022.101316.

Kumagai, Shogo, Jun Nakatani, Yuko Saito, Yasuhiro Fukushima, and Toshiaki Yoshioka. 2020. "Latest Trends and Challenges in Feedstock Recycling of Polyolefinic Plastics." *Journal of the Japan Petroleum Institute* 63 (6): 345–64. https://doi.org/10.1627/JPI.63.345.

Kunwar, Bidhya, H. N. Cheng, Sriram R. Chandrashekaran, and Brajendra K. Sharma. 2016. "Plastics to Fuel: A Review." *Renewable and Sustainable Energy Reviews* 54: 421–28. https://doi.org/10.1016/j.rser.2015.10.015.

Kunwar, Bidhya, Bryan R. Moser, Sriraam R. Chandrasekaran, Nandakishore Rajagopalan, and Brajendra K. Sharma. 2016. "Catalytic and Thermal Depolymerization of Low Value Post-Consumer High Density Polyethylene Plastic." *Energy* 111: 884–92. https://doi.org/10.1016/j.energy.2016.06.024.

Kusenberg, Marvin, Azd Zayoud, Martijn Roosen, Hang Dao, Mehrdad Seifali Abbas-abadi, Andreas Eschenbacher, Uros Kresovic, Steven De Meester, and Kevin M Van Geem. 2022. "A Comprehensive Experimental Investigation of Plastic Waste Pyrolysis Oil Quality and Its Dependence on the Plastic Waste Composition." *Fuel*

Processing Technology 227 (September 2021): 107090.
https://doi.org/10.1016/j.fuproc.2021.107090.

Lei, Junxi, Guoan Yuan, Piyarat Weerachanchai, Shao Wee Lee, Kaixin Li, Jing Yuan
Wang, and Yanhui Yang. 2018. "Investigation on Thermal Dechlorination and
Catalytic Pyrolysis in a Continuous Process for Liquid Fuel Recovery from Mixed
Plastic Wastes." *Journal of Material Cycles and Waste Management* 20 (1): 137–
46. https://doi.org/10.1007/s10163-016-0555-3.

Li, X H, Y Z Meng, Q Zhu, and S C Tjong. 2003. "Thermal Decomposition
Characteristics of Poly (Propylene Carbonate) Using TG / IR and Py-GC / MS
Techniques" 81: 157–65. https://doi.org/10.1016/S0141-3910(03)00085-5.

Lin, Y. H., and H. Y. Yen. 2005. "Fluidised Bed Pyrolysis of Polypropylene over
Cracking Catalysts for Producing Hydrocarbons." *Polymer Degradation and
Stability* 89 (1): 101–8. https://doi.org/10.1016/j.polymdegradstab.2005.01.006.

Liu, Yirong, Jialin Qian, and Jianqiu Wang. 2000. "Pyrolysis of Polystyrene Waste in a
Fluidized-Bed Reactor to Obtain Styrene Monomer and Gasoline Fraction." *Fuel
Processing Technology* 63 (1): 45–55. https://doi.org/10.1016/S0378-
3820(99)00066-1.

Lopez, Gartzen, Maite Artetxe, Maider Amutio, Javier Bilbao, and Martin Olazar. 2017.
"Thermochemical Routes for the Valorization of Waste Polyolefinic Plastics to
Produce Fuels and Chemicals. A Review." *Renewable and Sustainable Energy
Reviews* 73 (November 2016): 346–68. https://doi.org/10.1016/j.rser.2017.01.142.

Lopez, Gartzen, Maite Artetxe, Maider Amutio, Gorka Elordi, Roberto Aguado, Martin
Olazar, and Javier Bilbao. 2010. "Recycling Poly-(Methyl Methacrylate) by
Pyrolysis in a Conical Spouted Bed Reactor." *Chemical Engineering and
Processing: Process Intensification* 49 (10): 1089–94.
https://doi.org/10.1016/j.cep.2010.08.002.

Mani, M., C. Subash, and G. Nagarajan. 2009. "Performance, Emission and Combustion
Characteristics of a DI Diesel Engine Using Waste Plastic Oil." *Applied Thermal
Engineering* 29 (13): 2738–44.
https://doi.org/10.1016/j.applthermaleng.2009.01.007.

Mastellone, M. L., F. Perugini, M. Ponte, and U. Arena. 2002. "Fluidized Bed Pyrolysis
of a Recycled Polyethylene." *Polymer Degradation and Stability* 76 (3): 479–87.
https://doi.org/10.1016/S0141-3910(02)00052-6.

Mastral, F. J., E. Esperanza, C. Berrueco, M. Juste, and J. Ceamanos. 2003. "Fluidized

Bed Thermal Degradation Products of HDPE in an Inert Atmosphere and in Air-Nitrogen Mixtures." *Journal of Analytical and Applied Pyrolysis* 70 (1): 1–17. https://doi.org/10.1016/S0165-2370(02)00068-2.

Mastral, J. F., C. Berrueco, and J. Ceamanos. 2007. "Modelling of the Pyrolysis of High Density Polyethylene. Product Distribution in a Fluidized Bed Reactor." *Journal of Analytical and Applied Pyrolysis* 79 (1-2 SPEC. ISS.): 313–22. https://doi.org/10.1016/j.jaap.2006.10.018.

Mastral, J. F., C. Berrueco, M. Gea, and J. Ceamanos. 2006. "Catalytic Degradation of High Density Polyethylene over Nanocrystalline HZSM-5 Zeolite." *Polymer Degradation and Stability* 91 (12): 3330–38. https://doi.org/10.1016/j.polymdegradstab.2006.06.009.

Mastral, José F., César Berrueco, and Jesús Ceamanos. 2006. "Pyrolysis of High-Density Polyethylene in Free-Fall Reactors in Series." *Energy and Fuels* 20 (4): 1365–71. https://doi.org/10.1021/ef060007n.

McAllister, Sara, Jyh-Yuan Chen, and A. Carlos Fernandez-Pello. 2011. *Fundamentals of Combustion Processes*. https://doi.org/10.1007/978-1-4419-7943-8.

Mertinkat, J., A. Kirsten, M. Predel, and W. Kaminsky. 1999. "Cracking Catalysts Used as Fluidized Bed Material in the Hamburg Pyrolysis Process." *Journal of Analytical and Applied Pyrolysis* 49 (1): 87–95. https://doi.org/10.1016/S0165-2370(98)00103-X.

Miandad, R., M. A. Barakat, Asad S. Aburiazaiza, M. Rehan, and A. S. Nizami. 2016. "Catalytic Pyrolysis of Plastic Waste: A Review." *Process Safety and Environmental Protection* 102: 822–38. https://doi.org/10.1016/j.psep.2016.06.022.

Miller, Steve, Naresh Shah, and Gerald P. Huffman. 2005. "Conversion of Waste Plastic to Lubricating Base Oil." *NPRA International Lubricants and Waxes 2005 Meeting Papers* 2005 (8): 1580–86.

Milne, Bruce J., Leo A. Behie, and Franco Berruti. 1999. "Recycling of Waste Plastics by Ultrapyrolysis Using an Internally Circulating Fluidized Bed Reactor." *Journal of Analytical and Applied Pyrolysis* 51 (1): 157–66. https://doi.org/10.1016/S0165-2370(99)00014-5.

Miskolczi, N., A. Angyal, L. Bartha, and I. Valkai. 2009. "Fuels by Pyrolysis of Waste Plastics from Agricultural and Packaging Sectors in a Pilot Scale Reactor." *Fuel Processing Technology* 90 (7–8): 1032–40.

https://doi.org/10.1016/j.fuproc.2009.04.019.

Miskolczi, Norbert, Laszlo Bartha, and Andras Angyal. 2006. "High Energy Containing Fractions from Plastic Wastes by Their Chemical Recycling." *Macromolecular Symposia* 245–246: 599–606. https://doi.org/10.1002/masy.200651386.

Miskolczi, Norbert, Chunfei Wu, and Paul T. Williams. 2016. "Fuels by Waste Plastics Using Activated Carbon, MCM-41, HZSM-5 and Their Mixture." *MATEC Web of Conferences* 49: 1–6. https://doi.org/10.1051/matecconf/20164905001.

Moorthy, Krishna, Venkateswarlu Chintala, Amit Sharma, Shashank Pal, Jitendra K Pandey, and Praveen Ghodke. 2020. "Review of Catalyst Materials in Achieving the Liquid Hydrocarbon Fuels from Municipal Mixed Plastic Waste (MMPW)." *Materials Today Communications* 24 (February): 100982. https://doi.org/10.1016/j.mtcomm.2020.100982.

Murata, Katsuhide, Mihai Brebu, and Yusaku Sakata. 2009a. "The Effect of PVC on Thermal and Catalytic Degradation of Polyethylene, Polypropylene and Polystyrene by a Continuous Flow Reactor." *Journal of Analytical and Applied Pyrolysis* 86 (1): 33–38. https://doi.org/10.1016/j.jaap.2009.04.003.

Singh, R. K., Biswajit Ruj, A. K. Sadhukhan, and P. Gupta. "Thermal Degradation of Waste Plastics under Non-Sweeping Atmosphere: Part 1: Effect of Temperature, Product Optimization, and Degradation Mechanism." Journal of Environmental Management 239, no. March (2019): 395–406. https://doi.org/10.1016/j.jenvman.2019.03.067.

Murata, Katsuhide, Mihai Brebu, and Yusaku Sakata. "The Effect of Silica-Alumina Catalysts on Degradation of Polyolefins by a Continuous Flow Reactor." Journal of Analytical and Applied Pyrolysis 89, no. 1 (2010): 30–38. https://doi.org/10.1016/j.jaap.2010.05.002.

Murata, Katsuhide, Y. Hirano, Y. Sakata, and Md Azhar Uddin. 2002. "Basic Study on a Continuous Flow Reactor for Thermal Degradation of Polymers." *Journal of Analytical and Applied Pyrolysis* 65 (1): 71–90. https://doi.org/10.1016/S0165-2370(01)00181-4.

Murata, Katsuhide, Yusaku Sakata, and Mihai Brebu. 2022. "Thermal Degradation of Polyethylene in the Presence of a Non-Acidic Porous Solid by a Continuous Flow Reactor." *Journal of Analytical and Applied Pyrolysis* 161 (November 2021): 105395. https://doi.org/10.1016/j.jaap.2021.105395.

Neves, Isabel C., Gabriela Botelho, Ana V. Machado, and Patrícia Rebelo. 2007.

"Catalytic Degradation of Polyethylene: An Evaluation of the Effect of Dealuminated Y Zeolites Using Thermal Analysis." *Materials Chemistry and Physics* 104 (1): 5–9. https://doi.org/10.1016/j.matchemphys.2007.02.032.

Orozco, Santiago, Jon Alvarez, Gartzen Lopez, Maite Artetxe, Javier Bilbao, and Martin Olazar. 2021. "Pyrolysis of Plastic Wastes in a Fountain Confined Conical Spouted Bed Reactor: Determination of Stable Operating Conditions." *Energy Conversion and Management* 229: 113768. https://doi.org/10.1016/j.enconman.2020.113768.

Pacheco-López, Adrián, Fabian Lechtenberg, Ana Somoza-Tornos, Moisès Graells, and Antonio Espuña. 2021. "Economic and Environmental Assessment of Plastic Waste Pyrolysis Products and Biofuels as Substitutes for Fossil-Based Fuels." *Frontiers in Energy Research* 9 (June): 1–14. https://doi.org/10.3389/fenrg.2021.676233.

Panda, Achyut K., R. K. Singh, and D. K. Mishra. 2010. "Thermolysis of Waste Plastics to Liquid Fuel. A Suitable Method for Plastic Waste Management and Manufacture of Value Added Products-A World Prospective." *Renewable and Sustainable Energy Reviews* 14 (1): 233–48. https://doi.org/10.1016/j.rser.2009.07.005.

Papari, Sadegh, Hanieh Bamdad, and Franco Berruti. 2021. "Pyrolytic Conversion of Plastic Waste to Value-Added Products and Fuels: A Review." *Materials* 14 (10). https://doi.org/10.3390/ma14102586.

Park, Ki Bum, Yong Seong Jeong, Begum Guzelciftci, and Joo Sik Kim. 2019. "Characteristics of a New Type Continuous Two-Stage Pyrolysis of Waste Polyethylene." *Energy* 166: 343–51. https://doi.org/10.1016/j.energy.2018.10.078.

Park, Ki Bum, Yong Seong Jeong, Begum Guzelciftci, and Joo Sik Kim. "Two-Stage Pyrolysis of Polystyrene: Pyrolysis Oil as a Source of Fuels or Benzene, Toluene, Ethylbenzene, and Xylenes." *Applied Energy* 259, no. June 2019 (2020): 114240. https://doi.org/10.1016/j.apenergy.2019.114240.

Park, Ki Bum, Yong Seong Jeong, and Joo Sik Kim. 2019. "Activator-Assisted Pyrolysis of Polypropylene." *Applied Energy* 253 (May): 113558. https://doi.org/10.1016/j.apenergy.2019.113558.

Park, Ki Bum, Seung Jin Oh, Guzelciftci Begum, and Joo Sik Kim. 2018. "Production of Clean Oil with Low Levels of Chlorine and Olefins in a Continuous Two-Stage Pyrolysis of a Mixture of Waste Low-Density Polyethylene and Polyvinyl Chloride." *Energy* 157: 402–11. https://doi.org/10.1016/j.energy.2018.05.182.

Peng, Yujie, Yunpu Wang, Linyao Ke, Leilei Dai, Qiuhao Wu, Kirk Cobb, Yuan Zeng, Rongge Zou, Yuhuan Liu, and Roger Ruan. 2022. "A Review on Catalytic Pyrolysis of Plastic Wastes to High-Value Products." *Energy Conversion and Management* 254 (January): 115243. https://doi.org/10.1016/j.enconman.2022.115243.

Phyllis2. 2022. "ECN Phyllis Classification-Plastics." 2022. https://phyllis.nl/Browse/Standard/ECN-Phyllis#plastic.

PlasticEurope. 2021. "Plastics - the Facts." Brussels. https://plasticseurope.org/knowledge-hub/plastics-the-facts-2021/.

Predel, M., and W. Kaminsky. 2000. "Pyrolysis of Mixed Polyolefins in a Fluidized-Bed Reactor and on a Pyro-GC/MS to Yield Aliphatic Waxes." *Polymer Degradation and Stability* 70 (3): 373–85. https://doi.org/10.1016/S0141-3910(00)00131-2.

Qureshi, Khan Muhammad, Andrew Ng Kay Lup, Saima Khan, Faisal Abnisa, and Wan Mohd Ashri Wan Daud. 2018a. "A Technical Review on Semi-Continuous and Continuous Pyrolysis Process of Biomass to Bio-Oil." *Journal of Analytical and Applied Pyrolysis* 131 (December 2017): 52–75. https://doi.org/10.1016/j.jaap.2018.02.010.

Qureshi, Khan Muhammad, Andrew Ng Kay Lup, Saima Khan, Faisal Abnisa, and Wan Mohd Ashri Wan Daud. "A Technical Review on Semi-Continuous and Continuous Pyrolysis Process of Biomass to Bio-Oil." *Journal of Analytical and Applied Pyrolysis* 131, no. December 2017 (2018): 52–75. https://doi.org/10.1016/j.jaap.2018.02.010.

Qureshi, Muhammad Saad, Anja Oasmaa, Hanna Pihkola, Ivan Deviatkin, Anna Tenhunen, Juha Mannila, Hannu Minkkinen, Maija Pohjakallio, and Jutta Laine-ylijoki. 2020. "Journal of Analytical and Applied Pyrolysis Pyrolysis of Plastic Waste : Opportunities and Challenges" 148 (February).

Remedio Hernández, Maria Del, Ángela N. García, and Antonio Marcilla. 2005. "Study of the Gases Obtained in Thermal and Catalytic Flash Pyrolysis of HDPE in a Fluidized Bed Reactor." *Journal of Analytical and Applied Pyrolysis* 73 (2): 314–22. https://doi.org/10.1016/j.jaap.2005.03.001.

Saad, Juniza Md, Paul T. Williams, Ye Shui Zhang, Dingding Yao, Haiping Yang, and Hui Zhou. 2021. "Comparison of Waste Plastics Pyrolysis under Nitrogen and Carbon Dioxide Atmospheres: A Thermogravimetric and Kinetic Study." *Journal*

of *Analytical and Applied Pyrolysis* 156 (May): 105135.
https://doi.org/10.1016/j.jaap.2021.105135.

Salaudeen, Shakirudeen A., Sultan M. Al-Salem, Sonu Sharma, and Animesh Dutta. 2021. "Pyrolysis of High-Density Polyethylene in a Fluidized Bed Reactor: Pyro-Wax and Gas Analysis." *Industrial and Engineering Chemistry Research* 60 (50): 18283–92. https://doi.org/10.1021/acs.iecr.1c03373.

Scheirs, John. 2006. *Overview of Commercial Pyrolysis Processes for Waste Plastics*.

Scott, D. S., S. R. Czernik, J. Piskorz, and D. St A.G. Radlein. 1990. "Fast Pyrolysis of Plastic Wastes." *Energy and Fuels* 4 (4): 407–11. https://doi.org/10.1021/ef00022a013.

Seo, Young Hwa, Kyong Hwan Lee, and Dae Hyun Shin. 2003. "Investigation of Catalytic Degradation of High-Density Polyethylene by Hydrocarbon Group Type Analysis." *Journal of Analytical and Applied Pyrolysis* 70 (2): 383–98. https://doi.org/10.1016/S0165-2370(02)00186-9.

Serrano, D. P., J. Aguado, J. M. Escola, and E. Garagorri. 2001. "Conversion of Low Density Polyethylene into Petrochemical Feedstocks Using a Continuous Screw Kiln Reactor." *Journal of Analytical and Applied Pyrolysis* 58–59: 789–801. https://doi.org/10.1016/S0165-2370(00)00153-4.

Silva, Bruno J.B., Lenivaldo V. Sousa, Lais R.A. Sarmento, Soraya L. Alencar, Paulo H.L. Quintela, and Antonio O.S. Silva. 2020. "Kinetic Study of Thermocatalytic Degradation of UHMWPE over Microporous and Hierarchical ZSM-23 Zeolite." *Applied Catalysis B: Environmental* 267 (October 2019): 118699. https://doi.org/10.1016/j.apcatb.2020.118699.

Singh, R. K., B. Ruj, A. K. Sadhukhan, and P. Gupta. 2020. "A TG-FTIR Investigation on the Co-Pyrolysis of the Waste HDPE, PP, PS and PET under High Heating Conditions." *Journal of the Energy Institute* 93 (3): 1020–35. https://doi.org/10.1016/j.joei.2019.09.003.

Singh, R. K., Biswajit Ruj, A. K. Sadhukhan, P. Gupta, and V. P. Tigga. 2020. "Waste Plastic to Pyrolytic Oil and Its Utilization in CI Engine: Performance Analysis and Combustion Characteristics." *Fuel* 262 (May 2019): 116539. https://doi.org/10.1016/j.fuel.2019.116539.

Soudais, Yannick, Ludivine Moga, Jaroslav Blazek, and Florent Lemort. 2007. "Coupled DTA-TGA-FT-IR Investigation of Pyrolytic Decomposition of EVA, PVC and Cellulose." *Journal of Analytical and Applied Pyrolysis* 78 (1): 46–57.

https://doi.org/10.1016/j.jaap.2006.04.005.

Sunaryo, Marwan Efendy, Sarjito, and Nur Saifullah Kamarrudin. 2019. "Pyrolysis of Plastic Waste as an Alternative Fuels in Spark Ignition Engine." *International Journal of Emerging Trends in Engineering Research* 7 (11): 454–59. https://doi.org/10.30534/ijeter/2019/097112019.

Vempatapu, Bhanu Prasad, and Pankaj K. Kanaujia. 2017. "Monitoring Petroleum Fuel Adulteration: A Review of Analytical Methods." *TrAC - Trends in Analytical Chemistry* 92: 1–11. https://doi.org/10.1016/j.trac.2017.04.011.

Vollmer, Ina, Michael J.F. Jenks, Mark C.P. Roelands, Robin J. White, Toon van Harmelen, Paul de Wild, Gerard P. van der Laan, Florian Meirer, Jos T.F. Keurentjes, and Bert M. Weckhuysen. 2020. "Beyond Mechanical Recycling: Giving New Life to Plastic Waste." *Angewandte Chemie - International Edition* 59 (36): 15402–23. https://doi.org/10.1002/anie.201915651.

Walendziewski, Jerzy. 2005. "Continuous Flow Cracking of Waste Plastics." *Fuel Processing Technology* 86 (12–13): 1265–78. https://doi.org/10.1016/j.fuproc.2004.12.004.

Westerhout, R. W.J., J. Waanders, J. A.M. Kuipers, and W. P.M. Van Swaaij. 1998a. "Development of a Continuous Rotating Cone Reactor Pilot Plant for the Pyrolysis of Polyethene and Polypropene." *Industrial and Engineering Chemistry Research* 37 (6): 2316–22. https://doi.org/10.1021/ie970703y.

Williams, Elizabeth A., and Paul T. Williams. 1997. "Analysis of Products Derived from the Fast Pyrolysis of Plastic Waste." *Journal of Analytical and Applied Pyrolysis* 40–41: 347–63. https://doi.org/10.1016/S0165-2370(97)00048-X.

Williams, P. T., and E. A. Williams. 1999. "Product Composition from the Fast Pyrolysis of Polystyrene." *Environmental Technology (United Kingdom)* 20 (11): 1109–18. https://doi.org/10.1080/09593332008616908.

Williams, Paul T, and Elizabeth A Williams. 1999. "Fluidised Bed Pyrolysis of Low Density Polyethylene to Produce Petrochemical Feedstock" 51: 107–26.

Xu, Fanfan, Bo Wang, Dan Yang, Junhui Hao, Yingyun Qiao, and Yuanyu Tian. 2018. "Thermal Degradation of Typical Plastics under High Heating Rate Conditions by TG-FTIR: Pyrolysis Behaviors and Kinetic Analysis." *Energy Conversion and Management* 171 (April): 1106–15. https://doi.org/10.1016/j.enconman.2018.06.047.

Yang, Ren-Xuan, Kalsoom Jan, Ching-Tien Chen, Wan-Ting Chen, and Kevin C.-W.

Wu. 2022. "Thermochemical Conversion of Plastic Waste into Fuels, Chemicals, and Value-added Materials: A Critical Review and Outlooks." *ChemSusChem*. https://doi.org/10.1002/cssc.202200171.

Yildiz, Güray, Frederik Ronsse, and Wolter Prins. 2017. *Catalytic Fast Pyrolysis Over Zeolites*. https://doi.org/10.1039/9781788010245.Green.

Yoshioka, Toshiaki, Guido Grause, Christian Eger, Walter Kaminsky, and Akitsugu Okuwaki. 2004. "Pyrolysis of Poly(Ethylene Terephthalate) in a Fluidised Bed Plant." *Polymer Degradation and Stability* 86 (3): 499–504. https://doi.org/10.1016/j.polymdegradstab.2004.06.001.

Yuan, Haoran, Chengyu Li, Rui Shan, Jun Zhang, Yufeng Wu, and Yong Chen. 2022. "Recent Developments on the Zeolites Catalyzed Polyolefin Plastics Pyrolysis." *Fuel Processing Technology* 238 (October): 107531. https://doi.org/10.1016/j.fuproc.2022.107531.

Zayoud, Azd, Hang Dao Thi, Marvin Kusenberg, Andreas Eschenbacher, Uros Kresovic, Nick Alderweireldt, Marko Djokic, and Kevin M. Van Geem. 2022. "Pyrolysis of End-of-Life Polystyrene in a Pilot-Scale Reactor: Maximizing Styrene Production." *Waste Management* 139 (September 2021): 85–95. https://doi.org/10.1016/j.wasman.2021.12.018.

Zeaiter, J. 2014. "A Process Study on the Pyrolysis of Waste Polyethylene." *Fuel* 133: 276–82. https://doi.org/10.1016/j.fuel.2014.05.028.

Zeller, Michael, Niklas Netsch, Frank Richter, Hans Leibold, and Dieter Stapf. 2021. "Chemical Recycling of Mixed Plastic Wastes by Pyrolysis – Pilot Scale Investigations." *Chemie-Ingenieur-Technik* 93 (11): 1763–70. https://doi.org/10.1002/cite.202100102.

Zhao, Dongting, Xianhua Wang, James B. Miller, and George W. Huber. 2020. "The Chemistry and Kinetics of Polyethylene Pyrolysis: A Process to Produce Fuels and Chemicals." *ChemSusChem* 13 (7): 1764–74. https://doi.org/10.1002/cssc.201903434.