Waste Plastic Pyrolytic Catalysis

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With the increase in demand for plastic use, waste plastic (WP) management remains a challenge in the contemporary world due to the lack of sustainable efforts to tackle it. The increment in WPs is proportional to man's demand and use of plastics, and these come along with environmental challenges. This increase in WPs, and the resulting environmental consequences are mainly due to the characteristic biodegradation properties of plastics. Landfilling, pollution, groundwater contamination, incineration, and blockage of drainages are common environmental challenges associated with WPs. The bulk of these WPs constitutes polyethene (PE), polyethene terephthalate (PET) and polystyrene (PS). Pyrolysis is an eco-friendly thermo-chemical waste plastic treatment solution for valuable product recovery, preferred over landfilling and incineration solutions.

Keywords: Catalytic Pyrolysis ; Waste Plastic ; Heterogeneous Catalysts ; Biocatalysts

1. Introduction

Pyrolysis has continued to make waves in the plastic world, chemical, chemistry and biomedical industries for years now, with thermal pyrolysis serving as a fundamental process. Pyrolysis is defined as the thermal breakdown of organic materials upon heat application without the presence of oxygen or at reduced air conditions ^[1]. Operating temperatures linked to thermal pyrolysis with waste plastics as feedstock can reach up to 627 °C ^[2]. Demirbas ^[2] utilised a stainless-steel tube reactor to thermally pyrolyse municipal waste plastics (MWPs) of PE, PS, and polypropylene (PP) to produce gasoline range fuels. The reaction temperature ranges from about 280 °C to 627 °C. A reaction temperature of 627 °C is, no doubt, a massive quantum of heat energy and may not be economically viable, especially in the context of industrial-scale pyrolysis processes. High reaction temperatures, among other operating factors, pave the way to utilising catalysts to cut down on high energy inputs and product optimisation, among other reasons. As such, product quantity and quality can be affected. However, temperatures associated with thermal pyrolysis can fall to around 400–600 °C, an approximated temperature range utilised in work done by Zafar ^[3] to produce pyrolytic liquid fuel from waste plastics. The condition under which a catalyst is used to support thermal pyrolysis is referred to as catalytic pyrolysis or catalysis. Catalysts are known for their characteristic property of speeding up reaction processes. A catalyst can be any material that enhances a reaction rate without necessarily being used during the process ^[4].

Generally, pyrolysis is a process with huge potential leading to the production of valuable petrochemical products sourced from waste plastics and/or other organic materials. With this process, the reliability of petroleum/crude oil for energy generation can be reduced and/or altered. Additionally, with pyrolysis, the environmental challenges resulting from waste plastics can be addressed in an environmentally friendly manner. Unlike some other popular chemical processes, pyrolysis is eco-friendly, giving rise to alternative solutions with respect to landfilling and greenhouse gases reduction such as carbon-monoxide (CO) and carbon dioxide (CO₂) emissions. Butler et al. ^[5] showcased a typical case study wherein plastic constituents such as ethane, propane, naphtha, and gas oil (as in the case of benzene) were used to derive useful products. Some of these products include ethene, propene and benzene together with the final/intermediate products of PE, polyvinylchloride (PVC), PS and PP. All these products can serve as alternatives to conventional petroleum products and lessen dependability on them. As highlighted above, a range of petrochemical products can be produced with pyrolysis. To achieve this, pyrolysis operating parameters such as feedstock, reaction time, temperature, and catalysts, among other factors, are utilised. Pyrolysis that involves a feedstock without any catalyst can be considered as the baseline of the pyrolysis processes. Such pyrolysis is popularly referred to as thermal pyrolysis. Thermal pyrolysis can take different forms. For example, it can take the form of a co-pyrolysis. Co-pyrolysis involves a mixture of two or more feedstocks such as waste plastics and a biomass material under an inert atmosphere ^[6]. Sequential pyrolysis can be viewed as another form. This refers to a customised approach for the enhancement of formation rates of pyrolysis to be as direct and precise as possible, getting rid of imprecisions that may be due to variations in feedstock sample size [I]. Copyrolysis can be subjected to a sequential process. Sequential pyrolysis was utilised in research work carried out by Syamsiro et al. [8] to produce gasoline and diesel oil with MWPs as feedstock. Inarguably, MWPs are the major

components of municipal solid wastes (MSW). Demirbas ^[2] reported that PE and PP are the core constituents of MWP. In general, sequential pyrolysis of MWP or any of its respective composite waste plastics gives rise to pyrolysis optimisation. If aided with a catalyst, better-optimised results are obtained as shown in work by Syamsiro et al. ^[8]. Commercial Y-zeolite and natural zeolite catalysts are used with MWP ^[8]. These pyrolyses operate under inert conditions and can be subjected to a catalytic application, if necessary, for their optimisation and/or performance quality.

2. Catalytic Pyrolysis

Catalytic pyrolysis is chemical pyrolytic recycling that involves the addition of extra material(s), and catalyst gearing towards the handling of the feedstock (waste plastics in the case of polymeric pyrolysis of waste plastics) under inert conditions ^[9]. Catalytic pyrolysis, otherwise termed pyrolytic catalysis, significantly impacts various industries and disciplines. Pyrolytic catalysis is significant for benign process acquisition with reference to the pharmaceutical, material, and chemical industries ^[10]. This pyrolysis process constitutes catalytic degradation recycling that can yield higher quality products than those by thermal degradation when subjected to low temperatures ^[11]. As discussed above, research in pyrolysis has been conducted in the past, and it is believed further findings will be uncovered concerning catalyst types and quantity relevant to pyrolysis.

A range of catalysts is being developed and used. The most used catalysts include solid acid catalysts such as zeolite, silica-alumina, the Fluid Catalytic Cracking catalyst (FCC), Mobil Composition of Matter No. 41, MCM-41 [11][12][13][14], and bifunctional catalysts [15]. Largely, in the case of acidic catalyst degradation in relation to cracking reaction, the molecular weight of the polymer chain can be reduced rapidly, in which case carbonium ion intermediates switch hydrogen and carbon atom positions thereby producing isomers of high quality. This is evident in work done by Milne et al. [16]. Technically, this means that catalysts foster the optimisation of reactions and the resulting products. This gives rise to the effectiveness of other pyrolysis operating parameters. For example, Abnisa & Daud $\frac{6}{10}$ revealed that the presence of a catalyst in thermal pyrolysis could be a game-changer, with respect to the complexities of bio-oil yields, by significantly impacting HC chain lengths. Other research has shown and continues to show, that reducing the chain lengths of HC products impacts their heating temperature and, thus, affecting boiling point is one of the purposes of catalyst use. In a catalytic pyrolysis study done by Miandad et al. [17], liquid fuel oil produced with PS was produced in high yield with the support of a thermally activated modified natural zeolite (TA-NZ) catalyst. High yields of desired materials, improving miscibility with refinery streams, lowering pyrolysis reaction temperatures, and increasing chemical and physical stability are among the core reasons for the application of catalysts [18]. Catalysts with such characteristics are considered to be 'good'; but how is a catalyst determined by being 'good'? Adnan et al. [18], showed that approximately 100% attainment was possible with their zinc bulk catalysts (a heterogeneous catalyst). A response of such scale is undoubtedly a display of a 'good catalyst'. Understandably, a good catalyst shows high activity. Notably, high activity allows the use of comparatively small reactors and operations under reasonable conditions. This small size of reactors reflects optimisation, and certainly, activity plays a significant role in catalyst effects, as mentioned earlier. Nevertheless, activity is not the lone vital property of a 'good catalyst ^[19]. High selectivity for the desired products or yields is also important. To emphasise this, it is important that a catalyst retains its activity and selectivity for some time during the reaction process. Ideally, a catalyst does not change the total enthalpy and free energy of the reaction process ^[20]. Generally, the use of the catalyst is affected in this event, related to the rate of approach towards the end yield state of the reaction process. To date, it has been established that the type of catalyst used in pyrolysis can impact the type of catalytic pyrolysis process.

Broadly, catalysts can either be heterogeneous or homogeneous $\frac{[21]}{2}$. The size of these two types of catalysts is drawn (**Figure 1**) to reflect their use today, excluding biocatalysts. Foist $\frac{[22]}{2}$ discussed these two types of catalysts as being the sole types. However, a biocatalyst is another catalyst type that has arisen in the chemistry and chemical industries, and is a third type. Biocatalysts are highly influential in the food and medical industries, enzymes and cells being major constituents $\frac{[23]}{2}$.

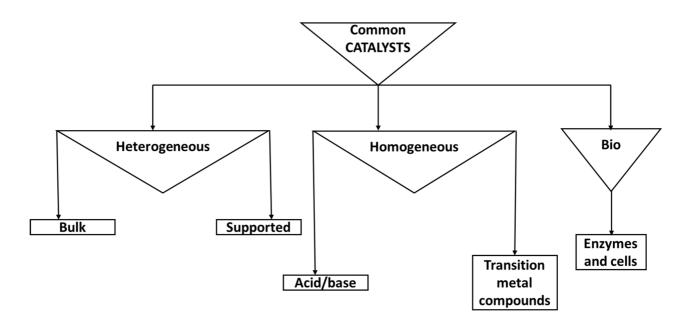


Figure 1. Common catalyst types- with emphasis on heterogeneous and homogeneous catalyses.

Catalysts involved in the depolymerisation of polymeric waste plastics allow the production of low molecular weight, highquality products, among other valuable materials. This is typical with homogeneous catalysts, generally divided into two forms. In processes involving this type of catalyst, the reactants, products, and catalyst(s) exist in the same phase. In contrast, heterogeneous catalysts are involved more in pyrolytic-based or gasification processes. It is vital to note that acidic/basic and transition metal compounds are not only applicable in gasification processes. Though not too common, or associated with the chemistry industry, other catalyst types are single-atom and green catalysts. In work by Farnetti et al. ^[21], another catalyst type, the heterogenised catalyst, is mentioned. This type of catalyst is known to function in the same phase (for homogeneous catalysts) or a dissimilar phase (heterogeneous or heterogenised) ^[21]. The practical benefits of these catalysts in the real world depend on their development, and modifications being done on them at the lab-scale. Catalytic pyrolysis has been adopted in developed countries to treat mixed waste plastics. This setup, a 'catalytic pyrolysis upgrade technique for fuel separation' is geared towards large-scale production and optimisation applications.

This process technique mainly encompasses a Knapper extrusion machine, pyrolysis reactor, catalytic upgrade reactor, fractionating tower, heating and temperature controller, separator for oil and water after condensation, and an oilcan. Together, these parts facilitate the pyrolysis process up to the separation of the fuel products. The waste plastic feedstock is fed into the extruder through the hopper by gravity and s mixed by shear heating, thereby converting the plastics into a melt for ease of pyrolysis. The plastic melt is then heated in the reactor under the influence of the catalyst. At this stage, the catalytic pyrolysis technique can be enhanced immensely. The limitations associated with WPTP is described by Yansaneh & Zein ^[24]. Limitations such as low quality and quantity yields, process optimisation, and reactor efficiency, among others, can be solved to a large extent using this upgrade technique. The fractionating tower separates useful products into columns after fuel gases are condensed by the condenser. Heavy factions occupy the bottom column, and gases (the lighter HCs) float on the top column. Heterogeneous catalysts are common and effective, as demonstrated by Wang et al. ^[25].

2.1. Heterogeneous Catalysts and Pyrolysis

The use of heterogeneous catalysts in pyrolysis is a promising technique that facilitates an increase of desired products at reduced temperatures ^[26]. These catalysts do not mix in their reaction with reactants (polymeric waste plastics) nor with their products. This means the phase of the catalyst is not the same as that of the reactants or products, enhancing their recovery from the medium of interaction, making such catalysts pivotal factors in chemical reactivity control ^[27]. This is unlike the case for homogeneous catalysts. Generally, heterogeneous catalysts are solid compounds added to another solid or liquid or gas compound in a reaction mixture, unlike homogeneous which are generally liquid or gas. This characteristic is key among other properties for their preference over homogeneous catalysts, especially for fuel oil and gas production in the chemical industry.

Empirically, heterogeneous catalysis is formed in various arrangements and is applicable to a variety of waste plastics, leading to the production of different products. Various research work in the past has used varieties of chemicals as catalysts for waste plastic recycling. In work by Adnan et al. ^[18], zinc bulk catalysts (Zn, ZnO and ZnCl₂) and zinc metal catalysts were applied to expanded PS waste plastics. Among these, zinc bulk catalyst and Zn metal proved the best per cost-effectiveness with liquid fuel yield starting at 350 °C. The Zn metal catalyst constituted 99.9% granules. The

heterogeneous catalysis of this catalyst led to the yield of liquid products, including the production of toluene and styrene monomers without mixing with the catalyst itself. This is an example of the schematic representation. Adnan et al. [28] used the same type of waste plastics as feedstock, as did Adnasn et al. [18]. However, in their work, the investigation included the influence and reactivity of PET on the pyrolysis of PS using an Al-Al₂O₃ crystalline catalyst. This had a particle size ≤0.44 mm fine powder upon mechanical grinding. Approximately 20% of Al-Al₂O₃ was used in the pyrolysis per feed:catalyst ratio to produce a range of useful compounds including styrene and benzene. The effects of this process were subjected to other factors such as decomposition temperature and reaction time. Hydrogen as an energy carrier was produced from waste plastics and biomass using Ni-CaO-C, a novel catalyst developed using mainly Ni, CaO and C, in a co-pyrolysis/gasification process ^[29]. With reference to the catalytic activity of Ni-CaO-C, the Ni load and support ratios were varied to facilitate H₂ production and CO₂ absorption capability. The novel catalyst was prepared using a pH method after careful comparative investigation with impregnation and sol-gel methods. In another study done by Wu et al. ^[30], hydrogen was generated with a catalyst but with a different source of plastic material, PE. The catalyst used was a coreshell catalyst (Ni-Ce@SiO₂), with the Ni-Ce core encapsulated in a silica shell to sinter the nanoparticles under increased temperature conditions. A cobalt oxide catalyst is another heterogeneous catalyst. Westerhaus et al. [31] used this catalyst in nitroarene reduction by pyrolysis, in which they reported a protocol for the preparation of their novel nanoscale cobalt oxide catalyst. They investigated a surface of carbon-nitrogen resulting in a significant yield of almost 100% with a conversion rate greater than 99%. This is a clear exhibition of superior reactivity.

In each of these catalysis studies, the catalysts did not mix with the reactants or the end products. Each kind of catalyst associated with heterogeneous catalysis is either bulk or supported. These 'supported catalysts' range from metals, oxides, sulphides, nitrides, and carbides. Aguado et al. [19] did similar research work with these kinds of catalysts, assigning them to eight groups. These include aluminium pillared clays, conventional acid solids, mesostructured catalysts, super-acid solids, gallosilicates, metals supported on carbon, basic oxides and, most importantly, nanocrystalline zeolites. Nanocrystalline zeolites are among the most widely studied catalysts in experimental research on polyolefin pyrolysis and the most widely used in the petrochemical industries ^[32]. The effect of temperature is a fundamental factor in catalytic behaviour. Research has shown that high temperature is hugely influential in regeneration and pyrolysis associated with zeolites, especially (ZSM-5), due to their bulk alignment of silica [32]. Catalysts in the bulk phase have the capability to favour oxidation processes. With reference to [33], in experimental work on cobalt oxide catalysts, a Powered X-Ray Diffraction (PXDR) device was utilised to study the behaviour of the oxidation state of the cobalt oxide catalyst under various reaction conditions during a chemical reaction. Zeolites have a porous structure and are acidic with the elemental ratio of Si/AI. This elemental ratio is significant in the classification of zeolites [34]. Beta zeolite (β -coop) and alpha cavity (α -cavity) are crucial to the classification of the porosity and acidity of zeolite catalysts. Faravelli et al. [35], and Kim [36] analysed the influential structural effects on pore openings in zeolites, with β -coop playing a strategic function. The β -coop of 6-openings gives rise to the formation of 12-ring pores, thereby establishing the channel wall of the catalyst, as shown in work done by Faravelli et al. [35], and Kim [36]. As such, 'other variant openings' of four, six, eight and ten rings can be generated from within the chemical structure of zeolites, in multiple factors of 2. This is the rationale supporting their characteristic mesh-like structure, especially at a molecular size, with larger particle sizes prevented from sieving through the pores onto waste plastics (such as PEs) to reduce their HC chains as in a pyrolytic reaction (hydrocracking). These openings are characterised by basic units known as rings, which may vary from one heterogeneous catalyst to the next.

Notably, Obeid et al. ^[37] used zeolite catalysts on PE waste plastic bottles in which the polymeric chains were shortened to $C_{10}-C_{28}$, and pyrolytic fuel-like products were obtained. This depicts the essence of zeolite application for fuel yield rather than as a chemical feedstock. This analysis categorises zeolite as a catalyst and the reason why zeolite is immensely applicable in petrochemical industries, as described by Maesen ^[32].

The application of zeolite catalysts, as with other popular heterogeneous catalysts such as proton exchanged zinc metal catalysts and silica-alumina or (MgO), can influence various products with different waste plastics.

2.2. Homogeneous Catalysts and Pyrolysis

Generally, and as mentioned above, heterogenous catalysts do not mix; unlike homogenous catalysts. This implies that homogeneous catalysts are in the same phase (liquid or gas) with the reactants in solution ^[38]. Keane ^[39] described a heterogenous catalyst as a substance that can uniformly dissolve in a reaction mixture in a gaseous or liquid solution. As mentioned earlier, homogeneous catalysts are typically liquid or gas compounds whose end reaction process results in a single phase. The result is a uniform reaction mixture with no distinct reactant showing. The resulting mixture of the two different liquid compounds ends up being uniform. Liquid 'A' reacting with liquid 'B' results in a miscible mixture of a single phase product 'C'. A Ni/SiO₂ aerogel is a homogeneous catalyst that Wang et al. ^[40] used in cracking an unknown quantity

of decane in a comparative investigation. Aerogel is applicable in research fields of photo-catalysis, methane reformation, and other catalysis-related activities ^{[41][42]}. The wide application of this catalyst is related to its textural properties such as large specific area, low density, high-temperature resistance and porosity.

Technically, there is a third phase (solid phase). Dorcheh & Abbasi ^[43], and Kakaei et al. ^[44] reported that some homogeneous catalytic reactions occur in the solid phase. This report contrasts with the report shared by Keane ^[39], as explained above and is in line with work by Kakaei et al. ^[44].

As reported by Casella ^[45], between 1993 and 2013, homogeneous catalysis experienced massive growth, with applicability to the polymerisation, organic synthesis, and pharmaceutical industries. This growth has continued to increase as pointed out in other research work including but not limited to, work carried out by Wang et al. ^[40] and Kakaei et al. ^[44].

Recovering the catalyst is typically complex or impossible because it is destroyed during the distillation process. There is no method of separation of the catalyst after the reaction. However, one big advantage of homogeneous catalysts is that they have significant contact with their reactants when the reaction is carried out. The role of the 'contact' and/or 'contact process' is key to the production of sulphuric acid (H_2SO_4), for instance. In fact, it is one of the most extensively utilised methods for its production ^[22].

2.3. Biocatalysts and their Reactions

Even though heterogeneous and homogeneous catalysts remain popular in the chemical industry, biocatalysts have substantial importance in industrial processes $[\underline{46}]$. The inroads biocatalysts continue to make are described in work by Kirimura & Ishii $[\underline{47}]$. They refer to these catalysts as power-tools on the basis of syntheses of organic materials with regards to selectivity. This selectivity is subject to the influence of process conditions and atmospheric environments. As the name implies, these catalysts are derived from biological materials such as living systems. Ali et al. $[\underline{48}]$ described naturally stirring lipases known for their ability to execute transesterification reactions significant in producing biofuels. These catalysts are used in the biotechnological industry, pharmaceutical and medical applications $[\underline{49}]$. Furthermore, they are applicable for uses such as the synthesis of drugs, biofuels, herbicides, cosmetics, food additives, among other substances $[\underline{50}]$.

Methane monooxygenase (MMO) is a natural biocatalyst. Muthudineshkumar & Anand ^[51] reported that MMO enzymes are well-known for the indirect conversion of methane to yield methanol under ambient pressure and temperature. This same report revealed that the production of methanol via the transition of methane upon the addition of MMO biocatalyst was a breakthrough in the methane conversion processes. Wilding & Micklefield ^[52] described biocatalysts, otherwise called enzymatic biocatalysts, as capable of facilitating the transformation of organic compounds. During these transformations of organic compounds in enzymatic reactions, other molecules are generated. When CO_2 is a by-product Wilding & Micklefield ^[52] define the enzyme as a decarboxylase. Note that the enzymes used in the preparation of biocatalysts can also include immobilised enzymes. In work by Vogt & Gerulis ^[10], on the synthesis of catalyst support for biofuel yield, the benefits of using immobilized (otherwise called encapsulated) biocatalysts, and are described along with catalytic reactions in general. Thus, immobilisation is pivotal in biocatalyst reactions. These immobilised enzymes can catalyse the production of good quality and unique chemicals, acclaimed for ease in product segregation and their property of being reused in consecutive processes ^[46].

Two or more enzymes reacting in a single carrier is a viable case, which, according to Pinheiro et al. ^[53], is termed coimmobilisation. This is believed to yield multifunctional biocatalysts. In the chemical world, specific reactions can give rise to co-immobilisation yields. Cascade reactions are known to yield products of co-immobilisation biocatalysts. This is supported by work by Pinheiro et al. ^[53] who described a process wherein the yield of the first reaction is the basematerial for the subsequent reaction and so on. Macromolecules that include amino acids are typical enzymatic catalysts.

Catalysis allows for further cracking of long-chain hydrocarbon materials, thereby reducing their boiling points for optimized yields ^[19] and the most favourable reaction times. The significance of this in industrial-scale operations is immense.

3. Future

Better output with pyrolytic catalysis, an optimal process to its thermal counterpart, is feasible for waste plastic management and pyrolytic product upgrade. The use of catalysts with waste plastic pyrolysis is investigated as more impactful than ordinary thermal cracking. Significant information is shared regarding the potential for converting waste

plastics, mixed waste plastics and a combination of waste plastics with other materials such as biomass into fuel fractions and other valuable products. The prominence of heterogeneous catalysis over homogeneous catalysis is widely discussed and their dominance in the economic world. The significance of other catalysts is also investigated. The future of this field is potentially informative.

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