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Catalytic Pyrolysis in Waste to Energy Recovery Applications: A Review

Oyetunji O. Oyeleke¹, Olayinka S. Ohunakin^{1,2}, Damola S. Adelekan¹

¹The Energy and Environment Research Group (TEERG), Mechanical Engineering Department, Covenant University, Ogun State, Nigeria

²Senior Research Associate, Faculty of Engineering & the Built Environment, University of Johannesburg, South Africa

Abstract-

The review examines the subject matter of catalytic pyrolysis, which is an upgrade on both the operation and output of the thermal pyrolysis process, capable of producing liquid oil products of a higher quality and yield compared to the thermal process, at reduced thermal and energetic demands. The use of catalysts plays a major role in increasing cracking activity and subsequent decomposition reactions, in attaining more desirable aromatic products. The properties, types, classes, loading mechanisms of catalyst as well as modification techniques are delved into in detail in asserting what makes catalyst efficient and effective in improving the pyrolysis process for different organic and inorganic feedstock materials. The catalytic pyrolysis of biomass substrates, which is an area less documented on was also examined, the effect of acidic zeolite catalyst on the process, mechanism, and end product of the pyrolysis process were examined in detail. Post-treatment techniques for the upgrading of liquid oil products were examined ranging from refining, filtration, distillation, and blending with conventional hydrocarbon fuels for use in different applications such as transport fuel deployment and utility generation.

Keywords: Pyrolysis, Catalyst, Plastic waste, Liquid oil

1 Introduction

The process of energy recovery from waste materials (organic and inorganic polymers) can be achieved through several chemical treatments and energy recovery technologies, ranging from gasification, hydrocracking, glycolysis, pyrolysis, etc., while several of these processes are tailored specifically to a particular type of waste feedstock, the pyrolysis process is versatile, not being limited to one type of raw material feedstock, as different materials both organic and inorganic can be thermally degraded through the process. The pyrolysis process involves the thermal decomposition of waste materials in the presence of an inert atmosphere at elevated temperatures to produce fuel resources, in form of liquid oil, solid char, and volatile gases, that are usable in energy-related applications such as heat generation, transport fuel, etc. [1]. These waste materials can vary from biomass, waste plastics, municipal solid waste (MSW), recycled waste, refuse-derived fuel (RDF), etc., making the pyrolysis process versatile, capable of adapting to different process and operational demands [2].

Therefore, the pyrolysis process is an efficient and sustainable treatment method with operational and environmental advantages, usable for different forms of waste feedstock, and can produce a wide range of high CV hydrocarbon compounds usable as fuel or chemical feedstock. The



pyrolysis process can be carried out via a thermal (conventional) or catalytic route; while the pyrolysis process itself is endothermic, the thermal route is one in which the process occurs unaided by any external agents, while the catalytic, involves the use of an external agent in aiding the pyrolysis process [3]. The catalytic process is used to overcome the challenges associated with the thermal pyrolysis process, mainly its high-temperature demand, up to 900C, and is thus an upgrade on it, usable to optimize process parameters, and obtain a better quality of end product, as the liquid product obtained from the thermal process contains long-chain carbons with low octane numbers, comparable to some conventional fuels, but may contain wax and different residues and impurities, thus needing further refinement to convert to usable products, dependent on factors such as the type of raw material feedstock, desired end product, as well as other process conditions [4].

As such, a wide variety of catalyst types are available based on the specific process needs and desired end product quantity, quality, and selectivity such as HZSM-5, ZSM-5, FCC, MCM-41, KSM, etc., and are capable of increasing the quality of the liquid oil by increasing the volume of lighter fractions in the oil, reducing the overall process energy requirements, as well as reducing the concentration of impurities [5]. The liquid oil obtained has the calorific potential to serve directly as alternative fuel sources or in blends with conventional fuel sources. This paper, therefore, reviews the influence, process, mechanism, and application of catalytic pyrolysis, the advantages conferred as well as the challenges associated, with a view of refining and improving its application, as well as the different types of catalysts, their respective properties, and effects on the end product selectivity i.e. quality and quantity of pyrolysis end products obtained.

2 Pyrolysis

As stated, the pyrolysis process is a chemical treatment avenue used for the thermal decomposition and cracking of polymeric materials with calorific potential, i.e. it involves the breaking down of long chain high molecular weight polymers to shorter, low weight molecular compounds, it occurs at elevated temperatures and in an inert environment to produce fuel products. The end products obtained are a combination of solid, liquid, and gaseous fractions. The pyrolysis process has the potential to convert over 78-84% of initial feedstock into liquid oil [1], [6], at an estimated theoretical energy consumption of 1.047-1.6MJ/Kg per Kg of feedstock [3], [7], at moderate temperatures between 500C to 700C.

There are several types of pyrolysis process reaction types including fast pyrolysis, slow pyrolysis, vacuum pyrolysis, etc., the most common are the fast and slow pyrolysis. In the fast pyrolysis process, the heating time of the feedstock to maximum temperature is smaller than the final residency time at that maximum temperature, implying a high heating rate, while for slow pyrolysis, the heating time of the feedstock to the maximum temperature, is longer than the residency time at the maximum intended temperature, implying the use of a low heating rate [4], [8]. The pyrolysis process is also influenced by several factors that can alter the phase, selectivity, quality, volume, and conversion efficiency of the end products, these include the heating rate, residency time, feedstock type and composition, particle size, process temperature, catalyst type, catalyst loading mechanism, moisture content, as well as temperature distribution within the reactor.

The pyrolysis process route can be thermal or catalytic, however, it should be noted that the use of catalysts as a factor is capable of significantly altering all other process factors and thereby holds a strong influence over all other factors.

3 Catalytic Pyrolysis

The catalytic pyrolysis process involves the use of an external agent (catalyst) to aid the thermal degradation reactions of the pyrolysis process, as these catalysts confer different advantages aimed at improving overall process and conversion efficiency by lowering the required activation energy needed and thus process temperature, as well as optimizing end product output, because the thermal pyrolysis process is more energy-intensive, as it can demand excessively high temperatures to produce quality end products which might not require any further upgrading. Catalytic pyrolysis, on the other hand, is capable of producing high yields of liquid fuel of low molecular weight, and higher quality at reduced thermal and energy demands at an estimated HHV of between 38-46MJ/Kg and density of 0.77-0.84Kg/cm³ [3], [9].

According to [7], who investigated the influence of catalyst on the catalytic and non-catalytic pyrolysis of a mixture of waste electrical and electronic equipment (WEEE), at different process temperatures of 400C, 600C, and 800C, using two zeolite catalyst (HZSM-5, HUSY), the results indicated that the yield of liquid oil obtained from catalytic pyrolysis using HZSM-5 at 400C was more than that of thermal pyrolysis carried out at excessive temperatures of 600C and 800C, with HZSM-5, having the highest overall yield, up to 93%, emphasizing the improved cracking ability and product yield using catalysts.

3.1 Catalyst

The use of a catalyst has numerous advantages, but serves two major purposes, firstly to the product, as catalysts can increase the quantity and quality of the desired end product by improving the production of aromatics in the oil, this is done by altering process parameters such as lowering process temperatures and residency time, improving cracking and decomposition reactions, stimulating isomerization reactions, enabling greater control of product selectivity to gasoline ranges, thereby improving end product and reducing the energy demand and secondly to the process, as catalyst improve overall process efficiency and energetic performance of the pyrolysis process [1], [10]. Also, according to [11], who noted that catalyst display high selectivity in the conversion of aliphatic hydrocarbons to cyclic hydrocarbon compounds and aromatics in liquid production which have high octane ratings.

Table 1: Comparison between Thermal and Catalytic pyrolysis

THERMAL PYROLYSIS	CATALYTIC PYROLYSIS
High energy demand	Reduced/less demand for energy
High-temperature demand	Reduced/less demand for temperature
The occurrence of impurities in liquid oil	Reduces impurities in liquid oil
High yield of liquid fraction with heavy oil	The decreased yield of liquid oil, but with low chain compounds
Yields liquid oil with low octane numbers	Yields liquid oil with high octane numbers
A higher quantity of solid char residue is obtained	Reduced quantity of solid char is produced

3.2 Catalyst Types

There are different types of catalysts available that serve different applications, dependent on desired end product selectivity and process requirements, they can be grouped as follows:

- FCC catalyst

- Mesoporous structured catalyst
- Metallic oxide catalyst
- Zeolites
- Silica-alumina catalyst
- Reforming catalysts

3.2.1. *FCC*

FCC catalysts are strong acidic catalysts, bonded by a non-zeolite with a zeolite crystal structure, having Lewis acid sites and Bronsted acid sites with ionizable hydrogen atoms serving as electron acceptors [3]. They are a form of silica-alumina catalysts. FCC's increase the yield of liquid products and decrease the yield of gaseous products, as they are heavily used in the petroleum industry in the production of liquid oil and gasoline from the cracking of heavy oil. The properties of FCC include its high activity, high surface area, large pore size, good thermal stability, and low coke formation, which facilitate the formation of low carbon number hydrocarbons [1]. FCC catalyst comprises four components including crystal zeolite, binder (silica sol), filler, and a refined alumina matrix structure.

3.2.2. *Zeolites*

Zeolites are crystalline aluminosilicate catalyst with a high internal 3D microporous structure having cavities and channels, where cations reside, the major characteristics of this catalyst are the open pores, pore size, pore distribution, uniform pore diameter, ion exchange capabilities, and acidic strength. They are categorized based on structure, which varies by several channel sizes such as (8-, 10-, 12-, 14-), as well as pore size (small, medium, and large). In the zeolite structure, there are two types of acidic sites, the Bronsted acidic site which is the main catalytic center, and the Lewis acidic sites. These two sites ensure zeolite catalysts have high acidity making them highly active in the cracking process, with the production of lighter olefins characterized by an increase in gaseous fraction and a decrease in the liquid fraction [3], [12]. They also display a high cracking rate, due mainly to its high pore surface area, which accelerates the thermal degradation reactions such as cracking, aromatization and isomerization processes, leading to an overall increase in volatile hydrocarbon compounds production [13], [14].

This coupled with its reduced rate of catalyst deactivation makes them highly suitable for pyrolysis and catalyst reuse. Examples include: microporous zeolites (HZSM-5, HUSY, HMOR, HY-zeolite) which are highly utilized in the degradation of polyolefin, the mesoporous zeolites (ZSM-5, MCM-22, ZSM-23, ZSM-11), and macroporous zeolites (H-beta-zeolite, SSZ-55, Y-zeolite) [10], [15], [16]. However, zeolite catalyst increases the ratio of branched carbon produced, while decreasing the production of straight-chain paraffin, therefore, acidic zeolite catalyst have been reported to be more effective in the pyrolysis of plastic waste and biomass (cellulose) compared to mesoporous and amorphous catalysts [1], but less effective for lignin (biomass) because zeolite micropores are smaller, while the molecules of lignin are large and bulky, thus making mass transfer and diffusion into pores of zeolites crystals difficult, this, in turn, leads to coke formation on the catalyst surface and deactivation, as molecules can't diffuse into the pores.

3.2.3. *Silica-alumina catalysts*

These are amorphous catalyst which increases the production of liquid oil and decrease the amount of gaseous product obtained, they also eliminate impurities by reducing the bromine contents of the liquid oil [3], [17].

3.2.4. *Reforming catalysts*

These are bi-functional catalysts which have different transition metals such as Co, Ni, Pt, and Mo, doped on the acidic sites of catalysts via wet impregnation to enhance the catalytic activity, they have a unique combination of acidic and metallic sites, and have bi-functional effects, favoring hydrogenation and dehydrogenation reactions at metallic sites, and isomerization reactions at acidic sites leading to the production of more aromatics [18]. Reforming catalyst show a high conversion yield and efficiency for plastic polymers to usable liquid oil as a result of its high acidity, as well as improved selectivity of end-products [3], [15].

3.2.5. *Mesoporous structured catalyst:*

These are porous silicate catalysts, having large surface areas, large pore sizes, and highly structured arrays of cylindrical mesopores, they essentially lack strong acidic sites, and are less active and display low catalytic activity compared to strong acid catalysts, examples such as MCM-41, MCM-48, KSF-16, and SBA-15 among others. However, they find application in catalytic pyrolysis involving large molecular-sized reactants and weak acidity demand, ensuring compound diffusion of reactant molecules through its larger pores, which results in a reduction in catalyst deactivation, applicable in bio-oil production from lignin biomass [12].

3.2.6. *Metal oxide catalyst:*

These are also referred to as **base catalysts** and are not as active as acidic catalysts, but still display an affinity for hydrogenation, isomerization, and alkylation reactions, they include FeO, CaO, ZnO, MgO, Al₂O₃, K₂CO₃, La₂O₃, Na₂CO₃, also two or more metal oxide catalysts can be mixed in their application to form hybrids, and they could also be utilized in the form of addition of a secondary catalyst phase to zeolite catalyst, which culminates in a strong change in catalyst acidity and improves selectivity for the pyrolysis end products [3]. This addition leads to new Lewis sites on the metal oxide phases which helps in reducing excessive cracking, and show good performance in cases of bio-oil production in deoxygenation and decarbonylation reactions, in which more monocyclic aromatics are formed, and less of polycyclic aromatics [19].

Of all these varying types of catalysts, the most commonly used are the zeolite catalysts due to its unique combination of key advantages such its pore size, acidic strength, and pore distribution, but catalyst selection is still subject to process demands, as different reactions and feedstock materials may demand a different type of catalyst.

3.3 *Classification of Catalysts*

Catalysts can be classified based on their phase as either homogenous or heterogeneous catalysts:

3.3.1 *Homogenous Catalyst*

This implies the catalyst is in a liquid phase and is applied directly to the waste feedstock, they confer unique advantages such as end product selectivity for the production of alkanes, and low process temperature [18], [21]. Examples include AlCl₃, ionic liquids, and metal tetrachloro-aluminates. However, the challenge of catalyst recovery and regeneration makes their usage less pronounced.

3.3.2 *Heterogeneous Catalyst*

This implies the catalyst is in a solid phase and can be applied either in direct contact or in vapour contact with the feedstock, heterogeneous catalysts are the most commonly used due to the ease of catalyst recovery and regeneration in both contact phases, as they are more easily separated and reused. They are mostly nanoscale acidic crystalline catalyst e.g. zeolite, silica-

alumina. Their large surface area and acidity influence selectivity towards the formation of lighter hydrocarbons [1]. Also, according to [20], heterogeneous catalysts are also able to withstand more stringent reaction conditions, reaching up to 1300C and 35MPa and allow for easy separation from end products.

3.4 Characteristics of Catalysts

There are certain characteristics and textural properties which determine the activity and thus selectivity of different catalysts usable for the pyrolysis process depending on the desired end product, they include crystalline structure and dimension, pore size and porosity, acidic strength, BET surface area, pore-volume, thermal stability, Si/Al ratio.

3.4.1 Crystalline structure and size

The high internal multi-dimensional crystalline structure of catalysts accelerate catalytic activity and decomposition reactions such as cracking as well as isomerization and aromatization reactions, while also increasing the production of aromatics in the liquid oil. Catalysts with multi-dimensions allow for more cracking compared to a mono-dimensional catalyst, as it provides more area available for cracking [3]. The crystalline size is dependent on and is a function of the Si/Al ratio, with crystal size increasing with increasing Si/Al ratio. Crystalline structure and size also determine the diffusion path, as the smaller path of small crystalline catalysts reduce coke formation [22].

3.4.2 Pore size and porosity

Secondary cracking of polymer occurs within the catalyst pores after primary cracking on the outer surface of the catalyst, while porosity influences the selective adsorption mechanism in catalytic pyrolysis. 2 types of pore sizes greatly influence the pyrolysis end product obtained, the microporous catalyst which favours the production of gases, with reduced produced of liquid oil, but of higher quality, while the macroporous catalyst favours increased liquid and char production, with less gas yield, therefore, porosity enhances the pyrolysis process, as the pore size and shape selectivity is crucial in aiding mass transfer and diffusion of large molecular weight compounds into the pores for conversion to small molecular weight aromatics. Pore size can also influence coke formation, as an inability for larger molecules to diffuse into smaller micropores can lead to coke formation on the catalyst surface, inadvertently leading to catalyst deactivation [9], [23].

3.4.3 Acidic strength

Acidic strength plays a major role in the pyrolysis process, as the acid sites present within the catalyst enhance the cracking process by increasing the yield of gaseous product obtained, while catalysts with high acidity also eliminate impurities from the liquid fuel produced, the acidity of a catalyst is measured by the Bronsted and Lewis acid sites present within the catalyst and is dependent on the strength, distribution, and density of these acidic sites the catalyst crystalline structure [11]. Bronsted sites are catalytically active in the formation of carbocations, which via β -scission results in the formation of olefin species. The number of acidic sites is proportional to the Si/Al ratio, with overall catalyst acidity increasing with Al^{3+} concentration in the catalyst framework.

Catalyst acidity determines the production of liquid fraction, as the higher the acidity, the lower the production of the liquid fraction [12], therefore an increase in liquid oil production can be achieved by using catalysts with low acidity, with howbeit lower quality. Acidic catalysts show a higher cracking rate in pyrolysis, as the acid sites influence β -scission reactions compared to

non-acidic or low acidic catalysts which increase aromatic (gasoline range) hydrocarbons in the liquid oil when condensed [24], [25].

3.4.4 BET surface area

A high surface area increases thermal cracking, as more area is available for cracking as primary cracking occurs on the catalyst outer surface, a high catalyst surface area also favours an increase in gas yields with a subsequent decrease in liquid yield [2].

3.4.5 Thermal stability

This property influences catalytic activity and stability of the catalyst at elevated temperatures ensuring proper control over product selectivity and distribution [24].

3.4.6 Si/Al ratio

This is a property that can be used to influence the acid density, reactivity, acidic strength, and the number of acid sites on different catalyst due to variations in the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, by increasing or decreasing the number of Si^{4+} or Al^{3+} sites, e.g. in zeolite catalysts, an increment of Al^{3+} increases the acid density, but decreases the acidic strength and vice versa, therefore, catalyst acidity increases with decreasing Si/Al ratio [2], [12].

3.5 Advantage of Catalytic Pyrolysis over Thermal Pyrolysis

The catalytic pyrolysis process possesses several advantages over the thermal process such as:

3.5.1 Increased conversion rates

Catalysts display a high conversion of large, long-chained aliphatic compounds to smaller aromatic compounds, this can also occur even at lower temperatures, thereby reducing energy input demand and thermal stresses induced on the walls of the reactor unit [15].

3.5.2 Quality of oil

The catalytic pyrolysis produces a higher quality of liquid oil (aromatic hydrocarbons $\text{C}_5 - \text{C}_{12}$) compared to the thermal process, which produces high carbon compounds from $\text{C}_5 - \text{C}_{28}$, as a result of an increase in the rate of decomposition reactions in which large chain heavy oil polymers are further broken down to smaller chain compounds, thus yielding a higher quality of liquid oil, as well as enabling a higher control of hydrocarbon production. Also, catalyst use enhances the conversion of heteroatoms into a gaseous state, which can be condensed down to a high-quality liquid. Physical properties such as viscosity are also affected, as the use of catalysts can reduce the viscosity of the liquid oil produced [3], [6], with the smaller and lighter hydrocarbon fractions produced from catalytic pyrolysis less viscous and thus suitable for engine performance, as highly viscous oil from thermal pyrolysis can negatively affect the engine performance

3.5.3 Removal of impurities

Catalyst can be used to reduce the concentration of impurities present in the pyrolysis end product such as nitrogen, Sulphur, phosphorus, and halogens in the liquid oil, while also assisting in removing oxygenated molecules in bio-oils, thereby increasing the HHV of the liquid oil, with metal-containing catalysts such as the reforming catalyst with acidic site doped metals showing an increased efficiency in removing impurities from the pyrolysis end product [26]. In the catalytic pyrolysis of RDF, the use of a catalyst decreased the production of less corrosive carboxylic acid [3].

3.5.4 Increased rate of reaction: the catalytic:

The higher conversion efficiency of feedstock can be attained with the catalytic conversion process, with a higher cracking rate observed even at reduced process temperatures [16].

3.5.5 Reduced process time and residency time:

The use of catalysts in pyrolysis reactions is capable of yielding similar end products at reduced process temperatures and residency time in the reactor when compared with the thermal pyrolysis process, thus making the process more economically feasible [11].

3.5.6 Reduced process temperature

The use of catalyst helps to lower the required pyrolysis temperature, which reduces the thermal and energy demand of the process, also culminating in reduced thermal stresses induced within the walls of the reactor unit, as opposed to the thermal pyrolysis process [9].

3.5.7 Increased calorific potential

Catalysts also assist in the removal of oxygenated molecules from the pyrolysis products which leads to an increase in the HHV of the liquid oil, while also reducing the moisture content and cetane index of the liquid product [16], catalysts such as zeolites are capable of reducing the pour point, density, flash point and boiling range of liquid oil [27].

3.6 Mechanism of Catalytic Pyrolysis

The mechanism of the catalytic decomposition varies, depending on the type of catalyst used, as the catalytic process is characterized by different reactions [26], and is strongly dependent on the acidity of the catalyst characterized by the Bronsted and Lewis acid sites on the catalyst, from catalytic cracking to isomerization and aromatization reactions. The initial and primary cracking occurs at the catalyst external surface, characterized by the degradation of high weight molecules to produce intermediates with different catalytic chemical reactions occurring at different sites such as hydrogenation and dehydrogenation reactions occurring at the metallic sites, while isomerization reaction occurs at the acidic sites, with strong Bronsted acidic sites needed for the catalytic cracking and formation of carbocations [3], [28]. Secondary cracking occurs at the internal porous structure of the catalyst for the selective decomposition of long-chain compounds to shorter compounds, with small pore sizes favoring the production of gases. Aromatization also starts at the acidic site of catalysts, which further leads to carbonation within hydrocarbons and the formation of olefins, these are then transformed on the catalyst acid sites (pores), into aromatic hydrocarbons via a series of processes consisting of oligomerization, cyclization, and hydrogen transfer reactions, the formation of aromatics is achieved via the Diels-Adler reaction.

It should be noted that at significantly higher temperatures, the liquid product starts to be converted to gases, with the gases also being subsequently stripped to form aromatics and char [29], evident by research studies indicating that at elevated temperatures, liquid yield decreases, with an increase in gas and solid char yield.

3.7 Catalyst Application Methodology

A majority of the challenges associated with the use of catalysts can be addressed with an effective catalyst loading methodology, as the catalyst can either be applied in a vapour contact phase or a direct contact (liquid) phase:

3.7.1 Direct contact phase (Liquid phase):

This involves the direct application of the catalyst with the feedstock in the reactor, for the thermal degradation process, this process is also referred to as the liquid phase, it has certain benefits to the pyrolysis decomposition process by improving energy efficiency, decreasing the overall process temperature as well as the residency time, however, there are certain drawbacks associated with this methodology involving catalyst recovery, characterized by the deposition of impurities on the catalyst surface such as chlorine, Sulphur, nitrogen, which then block the pores of the catalyst, which in turn limit its economic value and commercial application [27].

3.7.2 Indirect contact phase (Vapour phase):

This involves the indirect contact of the catalyst with the vapour produced from the pyrolysis process, characterized by a two-stage process involving a furnace unit for initial thermal degradation of feedstock, and then a separate reactor unit for catalytic cracking. The evolved pyrolyzed vapors from the furnace unit are then fed through the second stage reactor unit, ensuring no direct contact of catalyst and feedstock, ensuring efficient catalyst recovery, no coke formation, and reducing catalyst deactivation [1].

3.8 Challenges Associated With Use of Catalyst

3.8.1 Catalyst Loading:

Catalysts can be applied in different ways, the liquid and vapour contact phase, but in the liquid phase contact, in which the catalyst and polymers are mixed, the challenges encountered could be: possible catalyst deactivation which leads to a reduction of catalytic activity as a result of diffusion of the polymeric molecules into catalyst pores and difficulty in catalyst recovery [30].

3.8.2 Catalyst deactivation and coke formation:

The formation of coke and its subsequent deposition on the catalyst external surface leads to the deactivation of the active sites on the catalyst, reducing the yield of aromatics by impeding the diffusion and capillary flow of compounds. Coke formation occurs on the acidic sites of the external catalyst surface, depending on the catalyst topography and its textural characteristics. In addressing this, for FCC's the cracking catalyst which is frequently applied in large scale refineries can be regenerated, and also, possible hydrotreating of bio-oil has been reported to show positive results in catalyst recovery [20].

3.8.3 Catalyst Pore Size:

Catalyst pore size which is a geometric feature can also greatly influence the reactivity of the catalytic process, and product selectivity, according to [31], an increment in the pore size leads to increased hydrocarbon cracking to produce gases, however, large pore sizes have been reported to exhibit an initial high reactive activity, but afterward result in rapid deactivation, while catalyst with small pore sizes aids in preventing coke and carbonaceous depositions [32]. Catalysts with larger pore sizes also tend to possess lower acidic strength [9].

3.8.4 Catalyst short life-span:

Strong acidic catalysts with high density used in the direct contact method tend to possess a shorter lifespan as a result of coke formation, which leads to de-activation and thus would need to be constantly replaced. Furthermore, operational costs are also incurred as catalysts have limited lifespans outside of coke formations and must be periodically replaced [33].

3.9 Catalyst Modification

Different catalysts confer different advantages and enhance selective properties, and as such a rigorous criteria is employed in selecting a catalyst type for an operation. However, different types of catalyst possess different advantages, properties, and strength, therefore, the idea of catalyst modification was developed, as catalysts can also be modified to confer new properties, as well as improve its characteristics and efficiency to suit the needed pyrolysis operation and demand. This can be carried out in diverse techniques such as thermal and wet impregnation, acid leaching, and chemical liquid deposition (CLD) [11], [27]. According to [3], acid leaching by using HCl has been reported to remove impurities from the catalyst as well as increase its acidity, thermal impregnation involves the heating of the catalyst at elevated temperatures (over 500C) for a prolonged period (3hours), as this helps in eliminating volatile impurities present as well as increase catalyst activity. The wet impregnation technique is used to generate heterogeneous catalyst, an example of this are the reforming catalysts in which metals are doped on the acidic sites of silica-aluminates via wet impregnation.

Modified zeolite catalysts have an increased adsorption capacity, as the pores have been narrowed which increases the effective sieving effect, as it can only allow molecules of reduced size to pass through. According to [15], metal modified zeolite catalysts have been reported to increase the acidity and thus display increased catalytic activity and selectivity, with metals such as Mo, Ni, Co, Fe, Pb, etc. The reforming catalysts such as Cu^{2+} doped on the Al_2O_3 surface of silica-alumina have been reported to have increased surface area, pore size, and pore volume, which enhances overall catalytic activity and quality of the product obtained in obtaining higher yields of aromatic compounds.

In other cases, catalyst modification occurs on the catalyst surface alone to reduce coke formation which occurs on the external surface of the catalyst during fast pyrolysis operations, using chemical liquid deposition techniques (CLD), in which the external surface is modified without affecting the internal sites can be used to increase the yield of aromatics and reduce coke formation externally by reducing the number of external acid sites, with results ranging from a 25% increase in yield of aromatics, 17% increase in yield of olefins, and an 18% decrease in coke formation [15]. It involves covering the catalyst framework with modifiers such as SiO_2 , KH550, TEOS. [13], further discussed the need for catalyst modification, stating the need for dual catalysts or a catalyst with the unique combination of good acidic properties, hydrogenation properties, porosity, etc. which can also prevent deactivation and allow for re-use is desired.

3.10 CATALYTIC PYROLYSIS OF BIOMASS

As stated earlier, the pyrolysis process is versatile and can be applied to a wide range of waste feedstock materials, much has been documented on the pyrolysis of waste plastics, but the pyrolysis of biomass is an area less documented on, biomass encompasses wood substrates, agricultural waste (corn cob, rice husk, sugarcane bagasse, straw, etc.) [34]. Biomass resources have been reported to have advantages such as availability, CO_2 neutrality, making it the world's fourth-largest energy source, after coal, oil, and gas, with a reported supply allocation of 14% of the global energy consumption [35]. The biomass (triacylglyceride) feedstock structure consists of long polymeric chains, containing a unique macromolecules combination of either: cellulose, lignin, hemicellulose, and pectin, which affect the phase and quality of the end product obtained, as well as different reaction mechanisms for the pyrolysis of either cellulose and lignin, with

cellulose and hemicellulose yielding varying proportions of bio-oils over (72%) and non-condensable gases, while lignin gives less oil, gas and more bio-char [5], [20], [35]. The process occurs similarly in an inert atmosphere and at elevated temperatures from around 350C-550C, and in some cases reaching over 800C, with 400C-550C, being reported the optimized temperature range.

According to [8], the end-result of the biomass pyrolysis is a combination of either bio-char, bio-oil and gases, the proportion of which is dependent on process factors including: temperature, reaction time, heating rate etc., and the biomass feedstock, as the amount of volatile matter and ash content contained also affects the product yield, a high volatile content increases reactivity which favours yield of liquid product, while ash content favours char production, with bio-oil mainly obtained from cellulosic materials due to their high volatile content, and bio-char obtained from lignin, however, the bio-oil obtained contains high amounts of oxygenated content of about (35-60wt%), as well as other challenges such as its high moisture content, high acidity, low calorific and heating value, corrosiveness, low energy density, high viscosity, as the presence of oxygenates are drawbacks leading to issues of re-polymerization and phase separation leading to chemical instability in storage, thus prompting the investigation of catalysts into improving and upgrading the bio-oils obtained from the pyrolysis process, which has a LHV between 16.79-19MJ/Kg [2], [35].

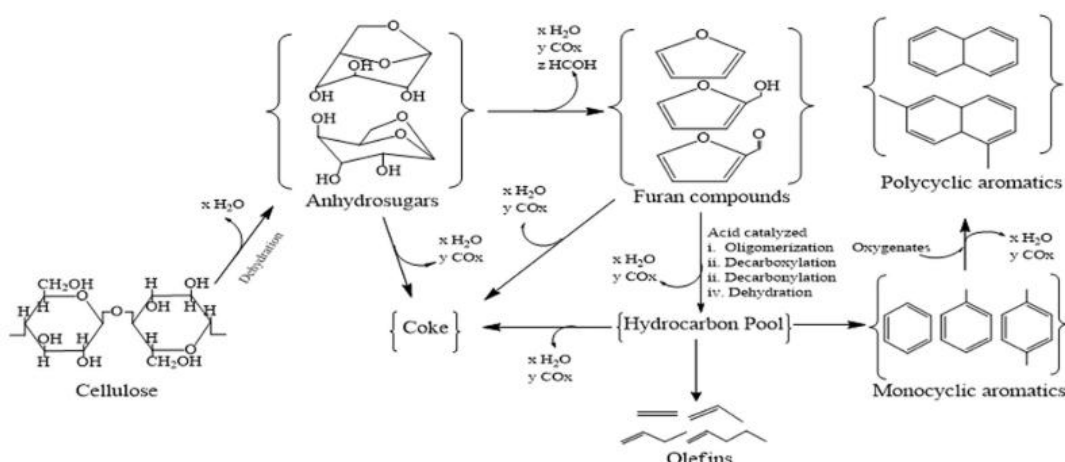
Several upgrading techniques such as steam reforming, hydro-deoxygenation (HDO), molecular distillation, esterification, emulsification to supercritical fluids [35], can be used, but are less pronounced due to several adverse effects on the system process. In particular, the catalytic pyrolysis of lignocellulosic biomass is optimized for the production of bio-oil, also known as pyrolysis oil, which is an organic liquid having several chemical constituents including ketones, acids, alcohols, aldehydes, esters, phenols, lignin-derived oligomers, and carboxylic oxygenates [17], [23], [34]. The use of heterogeneous catalysts serves as a means of improving the selectivity, calorific energy value, and quality of the bio-oil as well as reducing the oxygenates, thus catalytic fast pyrolysis of biomass has been studied using high acidic zeolite catalyst with varying pore sizes and acidic sites (HZSM-5) which favours the increased selectivity and yield of aromatic hydrocarbons as well as deoxygenation of oxygenates such as benzenediols, phenols, cresols, etc. from the pyrolytic vapors, as zeolite show better catalytic activity in the deoxygenation process and the prevention of re-polymerization of mono-cyclic aromatic compounds, in part due to its shape selectivity and acidity [15]. In overcoming issues related to catalyst deactivation and coke formation, metal modified zeolite catalyst which increases catalytic activity and product selectivity can be used containing metals Ni, Zn, Fe, Mo etc. doped on the surface [36].

The high ash content of some biomass substrates has been reported to pose a challenge in obtaining high-quality liquid products, especially from agricultural wastes which contain more ash content than wood. Several other techniques can be applied to improve the quality of the bio-oil from the thermal pyrolysis process, these sources range from hot gas filtration, acid washing, post pyrolysis filtering, and water leaching [20]. Therefore, catalytic fast pyrolysis serves as a means for the chemical stabilization, upgrading, and deoxygenation of bio-oils obtained from lignocellulosic biomass, and the product obtained can be used as a raw material for the chemical processing industry or as substitutes for heavy fuel in engines [11].

3.11 Mechanism of Catalytic Pyrolysis of Biomass (Cellulose)

The fast catalytic pyrolysis of biomass (cellulose) occurs over the zeolite catalyst, with the first stage occurring via catalytic cracking at the active acidic site of the catalyst (Bronsted site) involving the production carbocation (anhydrosugar) in the gas phase, from the heating and homogenous thermal decomposition of cellulose (lignin) through a process of acid-catalyzed dehydration in which scission of the C-C and C-O bonds occurs as well as side-chain scissions, the anhydrosugar obtained is relatively stable with no coke formation and undergoes further reactions including: dehydration, bond separation and re-arrangement in the presence of the zeolite catalyst, giving rise to furanic compounds (furfural, methyl-furan, furan-2-methanol), these compounds then diffuse into the catalyst acid pores and are adsorbed onto the acid sites for conversion to hydrocarbons via chemical reactions such as oligomerization, decarboxylation, decarbonylation and dehydration to form hydrocarbon pools (HCP) and olefins (C₂-C₆) [11], [37].

Decarboxylation, decarbonylation, and dehydration are deoxygenation reactions that occur at the active sites of catalysts, aimed at reducing the concentration of oxygenates. Via aromatization within the acidic pores of the catalyst and Diels-Alder condensation, these the desired end products of monocyclic aromatics and olefins are then obtained from the hydrocarbon pools, which can further reactions with oxygenates leading to the formation of polycyclic aromatics such as naphthalene which is an essential raw material in plastic polymer formation [15][36].



Fig

Figure 1: Aromatics formation via hydrocarbon pools using HZSM-5 zeolite in biomass [15]

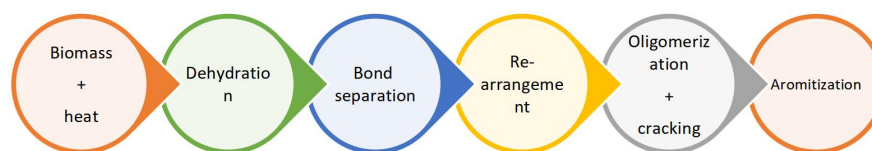


Figure 2: Catalytic process step reaction for lignocellulosic biomass

Recent advances in this field also involve the use of metal oxide modified zeolite catalysts such as ZnO-HZSM-5/MgO-HZSM-5, in which Bronsted sites are reduced, and more Lewis sites are formed which reduces excessive cracking as Bronsted sites are more catalytically active to reduce the formation of polycyclic aromatics and more of monocyclic aromatics, which have been reported to offer better deoxygenation properties and impart a higher energy value to the bio-oil

3.12 Upgrading and Application

The liquid oil obtained from catalytic pyrolysis despite being of high quality still requires some post-treatment processes to make them suitable for commercial applications in the case of automobile and transport fuel deployment, such as upgrading to improve octane ratings and eliminate impurities, filtration, distillation, and neutralization to improve the pH and reduce corrosiveness, before use with conventional motor engines, of which there are two techniques which can be applied: refining and blending with conventional hydrocarbon fuels, after which it can be used modified engines and generators and turbines [24]. In the case of blending bio-oil with conventional fuels, [20], obtained bio-oil from the catalytic fast pyrolysis of biomass and applied it with transport fuels in blends with ethanol up to 20%wt, it was documented to operate without any significant drop in engine performance up to 827C and 2.5MPa, in ethanol modified engines. The burning rate attained was close to 100%, with peak pressures even higher than standard. [38], reported the blending of liquid oil with conventional diesel at 20%wt and 40% distributions, and concluded that at 20%wt, successful operation of the engine was achieved in terms of thermal efficiency and exhaust emissions, however, a subsequent decrease in rated engine performance of 15%, was observed for 40% blends at higher RPMs of about 4000 rpm.

Conclusion

The pyrolysis process has been identified as a sustainable means for energy recovery from waste organic and inorganic materials to obtain useful hydrocarbons, of which there are two routes: the thermal and the catalytic. The catalytic pyrolysis process is a technique utilized in the efficient conversion of waste organic and inorganic materials into fuels and chemical feedstock using catalysts to aid the yield and selectivity of the products obtained as well as to optimize the pyrolysis process parameters and operation, it is thus an upgrade on the thermal pyrolysis process. The properties and effects of catalysts were examined in detail with the following conclusions emanating:

- The use of catalysts enhances the cracking process and can influence other key pyrolysis process factors and parameters.
- Different catalyst types exist, with varying properties, each imparting varying strengths, thus enhancing the liquid and gas yields, with some favoring liquid yield such as silica-alumina (MCM-41) and others gas yield such as zeolites (HZSM-5)
- Catalyst modification is an avenue less explored but is capable of imparting favorable properties to catalysts in meeting specific process and operational demands.
- Reforming catalysts with doped transition metals on an acidic catalyst sites show a higher degree of catalytic activity.
- The kinetic mechanism of the catalytic pyrolysis of biomass can follow several paths, depending on the variation of macromolecules (cellulose and hemicellulose) or lignin.
- Shape selectivity of catalyst plays an important role in the catalytic fast pyrolysis of biomass

- The fast pyrolysis process is ideal for pyrolysis in which the intended target is liquid oil and not char, and involves the use of a high heating rate.
- In the catalytic fast pyrolysis of biomass, (noble) metal-doped acidic catalyst has been reported to have better deoxygenation properties than the standard acidic catalyst
- While the upgraded oil from the catalytic fast pyrolysis of biomass contains less organic acids, phenolics, ketones, while aromatic and alkane content was reported higher and can be upgraded and used in blends with conventional hydrocarbon fuels.

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