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A Study on Thermo-Catalytic Degradation for Production of Clean Transport Fuel and Reducing Plastic Wastes

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Abstract

Both the landfilling and incineration processes of plastic waste management system are identified as sources of pollutant gas emitters. Reprocessing is also uneconomical in comparison to the virgin plastic products in terms of commercial values due to polymeric contamination. This article studies the thermo-catalytic conversion processes waste plastics. The reaction conditions and the quantification of types of catalysts used for the conversion processes influenced the quality of the resultant hydrocarbons. Obtaining higher yield of conversion and transport grade fuel require more investigation to adapt this technical process as one of the effective alternative resources for fuel production. Thermo-catalytic process resolves the problem of halogen contents in the PVC type plastics by converting them into residues with the use of NaHCO₃ and AgNO₃ which capture chlorine type products from the gaseous hydrocarbons. Addition of catalysts in the convenient reactor reduces the requirement of higher temperature operations like thermal cracking processes and produces more liquefied products. It has been observed that, the aromatic plastic contents should be observed during the conversion process to obtain fuels based on allowable aromatic contents according to the fuel standards and emission regulations implemented in respective regions. The temperature of the process need to be controlled as per the boiling points of the mixture contents to avoid formation of vapor in the reactor which could causes sticky adherence to the reactor walls. A continuous liquid fractionating distillation process can reduce the formation of light gases in the yield. It was also found that the mixture of LDPE, HDPE, PP and PS yield 87.19% fuel with 20 wt% ZnO catalyst at 200 – 400 °C in a steel reactor. These fuels can be used directly in the automotive engines or can be retreated in the refineries to divide into gasoline and diesel fuels as per carbon chains. Since the plastic feedstocks do not contain any sulfur components the produced fuel can be treated as clean enough. Thus the fuels produced from this process can be considered as one of the potential alternative resources of fuel production resulting into an effective reduction of plastic wastes in a country.

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1. Introduction

Plastic wastes can be turned into a valuable alternative resource of energy production. True recycling of waste materials, i.e. converting the wastes into useful products to be reused effectively, can cut down the net cost of waste collection, sorting and reprocessing [1]. Statistically, the average worldwide consumption of various types of plastics is almost found as 35% high-density polyethylene (HDPE), 23% polypropylene (PP), 10% polystyrene (PS), 13% polyvinyl chloride (PVC), 7% poly-ethylene terephthalate (PET), and 12% miscellaneous polymers. Due to special practices of consumers, polyolefin (PE and PP) and PS are the most prevailing plastics in the waste polymers' stream [2].

Nomenclature

ABS	Acrylonitrile-butadiene-styrene
PVC	Polyvinyl Chloride
ZSM	Zeolite Socony Mobil

Since most of the plastic products are thrown out after single use it has been significantly contributing the accretion of plastic solid wastes in earth. There are social, economic as well as political aspects of waste disposal systems along with the key technical challenges associated to the appropriate and efficient disposals. This is the reason why several different methods have been explored and applied to resolve the issues related to the polymer waste handling and disposal. From the very beginning of waste disposal activities, landfills dumping of all types of biodegradable and non-biodegradable wastes as well as incineration of combustible wastes are considered the mostly adopted processes. Both the landfilling and incineration processes of plastic wastes cause a loss of the available alternative energy resources. There are lot of direct, indirect, short or long term pollutions observed for these activities. These types of disposal processes are no longer encouraged in order to protect the environment. Numerous investigations on both the environmental and economic effect of various recycling processes have been conducting around the world. Since plastics are produced from petrochemical substances they have significant calorific values. Most of the consumed plastics possess more calorific values than few of the mostly used fuels like coal and gas (Table 1). That means the waste plastics can be used to recover energy [3].

Table 1. Heat capacity comparison between various plastics and other materials [4, 5]

Plastic Material	Heat capacity (MJ/kg)	Other materials	Heat Capacity (MJ/kg) [* MJ/m ³ @0°C]
PVC	18	Heavy fuel oil	41
PP	46.4	Petrol/Gasoline	44
PE	47	Coal	26
PET	46	Natural gas	36*
PS	41	Milled peat	10
ABS	35	Paper	17

According to forecasts, the consumption of plastics is increasing at a rate of 4-5% annually[2]. The recycling rates as well as the energy recovery of plastic wastes have been increasing and it is still wasting a lot of potential resources for energy recovery in the modern world. In reality, it needs about 7 yards of landfilling space to dump 1 ton of plastic wastes in the land [3]. Also recycling of plastic products can save about 80% of energy required to make products like bottle, containers and other items. As the energy economy is a great concern, such a waste of energy cannot be overlooked. For that reason, recycling of plastic wastes in the form of clean energy production

could be certainly an effective option. Thus the waste management complexities can be resolved. Though it requires a lot of techno-economic implementation, it is not an unattainable option [6].

Despite the implementation of various policies like clean environment, developed technologies and waste reduction, it is not likely that the volumes of plastic wastes will decline. New recycling methods will have to be developed. From the perspective of catalysis, chemical recycling of plastic wastes is the most noteworthy of plastic waste recovery techniques [4]. Though mechanical recycling can lead to recovery of plastic wastes effectively, it is restricted to the thermoplastics, homogeneity of the types, contamination level and colour similarity [4, 5]. For plastic producer, the quality and the stability of the reprocessed product is a major obstacle [7]. Presence of hazardous additives and impurities in the mixed plastic waste stream limits the reprocessing efficiency. There is possibility of incompliance with the food safety, medical instruments, and automobile equipment safety concern. Small amount of dissimilar resins can subjugate the commercial acceptance of the reprocessed plastics in compare to the virgin plastic made products. This recycling process cannot recover all the plastic wastes. The sorting of plastic wastes require more labour hours or sophisticated technological applications resulting increase of expenditure in the recovery process.

On the other hand, use of the plastic wastes as the source of feedstocks to produce fuels, monomers of the virgin plastics or various industrial chemicals have been considered as one of the most economic reprocessing options of waste management system. This process is also stated as tertiary or chemical recycling system. Based on the types of plastic wastes, various chemical or catalytic agents are used to obtain the desired products [5, 8]. Hydrogenation, gasification, chemical depolymerization, thermal treatments, catalytic cracking and reforming, etc. are considered as various types of feedstock based recycling process for plastic and rubber based wastes [5]. These recycling processes (i.e. both the mechanical and feedstock recycling) reduce the environmental pollution which could occur due to incineration and landfills [9]. Low temperature pyrolysis followed by a catalytic cracking, i.e. the continuous catalytic pyrolysis of HDPE gives more production of light olefins than the catalytic or pyrolysis process alone [10]. Similarly, Serrano et al. [11] investigated and found that two step processes could be adopted as one of the feasible technical processes to reduce waste plastics from the environment and produce transport grade fuels. In that case, among the various recycling methods of plastic wastes combination of the thermal cracking and catalytic cracking or the thermo-catalytic degradation are considered as commercially potential to obtain transport grade liquid fuels [11, 12]. There are still some techno-economic limitations for an efficient and complete recycling process development for waste plastics in terms of converting them into utile substances like liquid fuels.

This paper reviews the potential features of thermo-catalytic degradation of waste plastics as an alternative and effective way of waste reduction from environment. Also the potential of producing transport grade fuels following controlled process parameters of thermo-catalytic degradation has been reviewed. The usefulness of selective catalysts and their quantification, reaction temperature and the time to degrade the polymer into optimal liquid fuel yield has been discussed in brevity. It is expected that this potential technical process can be effectively utilized for commercial production of transport grade fuel and consequently plastic waste management system will be implemented in desired way.

2. Plastic waste management

Generally if the recycling is performed with the plastic products collected from the waste stream, they are not reused to produce the same product due to quality concerns [13]. Due to low grade utilization of the recycled plastic materials, alternative recycling processes are evaluated and further improvement is going on. Several preliminary issues have been discussed in this section so that the importance of the thermo-catalytic process can be perceived well.

2.1. Plastic wastes in Australia and USA

In case of Australia, the recycling rate of plastic wastes was 20.8% in the year 2012-2013 [14]. Out of total plastic consumption of 1.477 million tons, 307,300 tons were recycled (145,600 tons domestically and 161,800 tons sent to overseas). In USA, there were about 39.3 million tons of waste plastics generated in 2011[15]. It was nearly 11% of

the total municipal solid waste stream for that year. Of this total plastic wastes, 2.66 million tons (6.8%) were recycled, 3.9 million tons (9.9%) were converted to energy in waste-to-energy (WTE) plants, 0.27 million tons (0.7%) were used as alternative fuel in cement production, and the rest 32.5 million tons (82.7%) were dumped for landfills. Also, there were about 1.9 million tons of non-recyclable plastic wastes generated in the form of automotive shredder residue (ASR) [15]. Along with USA, Japan and Western Europe are also producing lot of waste plastics. China and India are also producing more and more waste plastics rapidly [16, 17]. Fig. 1 (adopted from [18]) represents the alarming track of plastic waste increment worldwide. Thus, plastic waste management and environment protection are key issues in everywhere in this world.

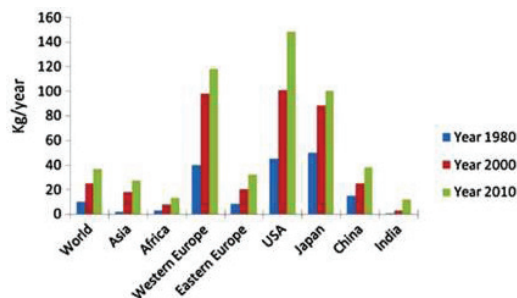


Fig.1. Regional per capita plastic consumption data (kg/year) [17]

2.2. Landfilling of plastic wastes

Waste plastics are not biodegradable; they remain for long period into the landfill. The lack of landfill sites and assessments of the environmental consequences of landfilling have led many countries to ban landfilling of combustible wastes, including wet organic waste [19, 20].

Landfilling of plastic wastes causes pollution by emitting toxic gases like furans and dioxins to the environment which are carcinogenic. Various types of additives, i.e. fillers, plasticizers, colorants are used with virgin plastics to make them user friendly, hygienic, durable, UV resistant and economic for the consumers. Hence, plastics can pollute the environment due to presence of various additives. Mostly Nonylphenols, Polybrominateddiphenyl ethers (PBDEs), di-(2-ethylhexyl) phthalate (DEHP), and BisphenolA (BPA), are mixed with the monomers of virgin plastics to act as catalyst in producing polymers and thus enhance other desired properties. Some of these used chemicals are found responsible as hormone-disrupters [21]. BisphenolA (BPA), which is extensively used with the epoxy resins of food and beverage containers and as monomer in the polycarbonate plastic of many consumer products, is alarmingly related to cardiac diseases, diabetes as well as abnormal increase of certain liver enzymes [22]. PBDEs may be responsible for lowering the immune system, thyroid disruptions, and troubles in fertility issues of human being. So, when plastics are used or discarded, the emissions based on these additives are undesirable from an environmental point of view [23]. The American Chemistry Council (ACC) reported that if all of the landfilled municipal solid wastes in USA could be diverted into waste to energy production processes it could reduce the coal consumption by 108 million tons. This is equivalent to the production of 162 million MWh of electricity for 16.2 Million households for one year [24]. Even the biodegradable plastics are liable for methane based greenhouse gas emission to the environment. Leachate forming is also another threat that can pollute the ground water being soaked by the soil.

2.3. Incineration of plastic wastes

On the other hand, incineration of wastes has been considered as the highly effective method to reduce the volume of wastes by producing energy. In most countries, it is the traditionally adopted technology. So, there is a widespread concern about the methodologies regarding incineration process and the emissions related to it. Air pollutants like CO, CO₂, NO_x, SO_x, particulate matters (PM), volatile organic compounds (VOCs), and polycyclic

aromatic hydrocarbons (PAHs) are found from the plastic waste incinerations [23, 25]. Almost 30% by weight of waste plastics are converted into CO₂ due to this process with a factor of 25 gm/MJ fuel to be compared with other fuels [26]. Though the incineration process converts the waste into energy for industrial uses in some extent, the conversion efficiency and the emitted pollutants are endangerment concerns. Plastic wastes are generally burnt for few seconds in high temperature (e.g. 2 sec, 850 OC or higher) incinerators with an excess air ratio between 1.0 and 1.8 [25, 27]. The ash by-products of incineration process are generally landfilled and are of risk based concerns due their carcinogenic threat [24]. Enforcement of new legislations, increased expense, social as well as ecological awareness, stringent strategies of environment protection, etc. are the restricting factors to the disposals of both organic as well as plastic wastes in the landfills and incinerators [28].

3. Thermo-catalytic degradation of plastic wastes

There is a significant difference between thermal and catalytic cracking processes – in terms of reaction condition, raw material feeding system and product output. Thermal cracking can be explained by a free radical mechanism [29] and the catalytic cracking can be recognized by carbonium ions [30] consisting of single positive charge carrier ions from the hydrocarbon. The controlled combination of these two processes helped reducing the process operation costs and increased the conversion efficiency along with the desired products [10-12, 28].

3.1. Thermal cracking (pyrolysis and liquefaction)

In the thermal cracking/pyrolysis process, the reaction is performed within the temperature region of 350-800 OC and the plastic materials are degraded in absence of both air/oxygen and catalysts [17]. The type of plastics or the mixture proportion of various plastic polymers governs the performance of the pyrolysis process along with the other parameters like temperature, reactors, residence time and product removal systems, heating rate, operating pressure, etc. [31]. The lighter molecular weight/less dense polymers require higher temperature in the pyrolysis process resulting in a wide range of hydrocarbons. Gases, light oils and chars are the main products of the process based on the governing parameters, which need further treatment (Condensation, Hydrotreating, Hydrocracking, Distillation, etc.) to convert into transport grade fuels. Typical pyrolysis features some drawbacks. Cooking of the reactor walls, sticking of plastics in the reactor walls are undoubtedly experienced in this process. As a result, the heat transfer efficiency is reduced resulting of fewer yields of liquid products (known as bio-oil). Periodic cleaning of the reactor becomes essential in such cases. Stirring of the molten polymers in the reactor as well as continuous removal of those molten polymers can resolve these obstacles in a large extent.

The thermal cracking process in presence of N₂ gas pressure system is termed as pyrolysis, whereas the similar reaction under H₂ gas pressure system is known as liquefaction [32]. Williams & Edward [32] conducted thermal cracking on various plastics under the experimental condition of 500^oC (@5^oC/min), type T316 stainless steel made bench top reactor of maximum pressure capacity 19.2 Mpa , 1 hour, 0.2-10Mpa of N₂ gas (for pyrolysis), 1 Mpa of H₂ gas (for liquefaction), etc. for the following observations (Table 2). This table infers that the liquefaction process yields less aromatic contents and produces more liquid substances. Hence the further treatment of producing the transport grade fuel from thermal cracking may be conducted with the liquefaction process if process expenditure is comparable. Also Zadogonkar&Umesh [33] described that the pyrolysis of PVC may emit toxic substances like polychlorinated dibenzodioxins (PCDD), polychlorinated dibenzofurans (PCDF), polychloro biphenyls (PCB) along the hydrochloric acid, which is corrosive. Both the higher amount of residues and the liquids of pyrolysis process have lower octane rating to be processed as transport grade fuel [17].

Baker [34] pointed out few issues about pyrolysis process of converting plastic wastes into fuel, which are: frequency of reactor chamber cleaning requirement is very high; poor heat conductivity within plastics; processing time increases with load in the chamber; high expenditure of consumable catalysts due to fouling; produced fuels lack tolerance to be suitably used in the engines or industrial machines instead of fossil fuels; flash point of the produced fuels are lower than that of diesel (45°C ~ 53°C) and usually vary in wide ranges (25°C ~ 45°C) due to presence of light hydrocarbons; and to perform as diesel fuel, the inventors have found that the fuel must be substantially rich in chains with a carbon chain length peaking around C16 (i.e. cetane). But removal of lighter

fraction hydrocarbon contents (5-7% wt) of boiling point lower than 160°C from the pyrolysis process outputs can lead to the improvement of flash point the fuel.

Table 2. Product yields of different thermal cracking processes

Plastic	Pyrolysis Process				Liquefaction Process			
	Oil (wt%)	Gas (wt%)	Residue (wt%)	Total aromatic and PAH compounds (wt%)	Oil (wt%)	Gas (wt%)	Residue (wt%)	Total aromatic and PAH compounds (wt%)
PE	93	7	0	16.4	95	5	0	15.5
PP	95	5	0	18.8	95	5	0	17.1
PS	71	2	27	100.0	77	2	22	100.0
PVC	-	-	-	-	2	38	52	52.7
PET	15	32	53	32.7	27	32	41	22.0
Waste DSD (mixed)	32.5	0.5	50.2	29.6	48.2	2.2	35.1	24.1
Waste Fost Plus (mixed)	64.1	4.3	23.3	27.6	70.6	4.9	17.8	24.9

Generally, the pyrolysis process operating on higher temperatures yields more gaseous and residues. The optimal working temperature zone of producing diesel or gasoline type liquid products is about 390–425 OC. Due to higher operating temperature, the composition of the yield products also changes into aromatic dominant than those of aliphatic compounds found in lower temperature [35, 36]. Both the residence time and the temperature of pyrolysis process control the quality of the yield product. Since the pyrolysis yields cannot be directly used as transport fuels, further improvement has been essential.

3.2. Catalytic and thermo-catalytic cracking

Catalysts help reducing the activation energy of the feedstock so that the required temperature in the thermal cracking process is reduced and the reaction rate is increased. Also the yield products are within the narrow range of hydrocarbons [37]. For instance, with various concentrations of SO₃ catalysts in the catalytic pyrolysis reaction of HDPE, the activation energies of HDPE, HDPE+3.5%SO₃ and HDPE+7%SO₃ are 342.95, 159.96, 132.61 KJmol⁻¹ respectively [38]. The boiling point of the gasoline, diesel, heavy oils and waxes ranges from 50-220 OC, 220-340 OC, 340-420 OC, 420-480 OC respectively. But the volatility of the compounds obtained from pyrolysis of various waste plastic products range widely. To obtain clean and stabilized petroleum fuel, the pyrolytic syngas and oils are treated in further stages [18]. Silica-alumina and the zeolites are mostly used to change both the volatility and nature of product of the pyrolytic oils [39]. Also the reactive acidic components of the pyrolytic oils can be eliminated by using Na-zeolite or aluminated MCM-41 catalysts. The Na-zeolites can effectively perform the de-halogenation of pyrolytic oils obtained from the halogenated plastics or electronic wastes [39]. With increasing number of acid sites, the level of the catalyst activity in polyolefin pyrolysis also increases. Zeolite-based catalysts due to their high acid strength achieve higher conversion than nonzeolitic catalysts [9].

Catalysts can be introduced into the reactors by either mixing the liquid form with the plastics before reaction occurs or mixing as vapor in the volatile fraction stream of pyrolysis or gasification processes [17]. Either of the processes is effective in terms of liquid yield. The ratio between catalyst and the polymer waste also controls the liquid fuel conversion efficiency of the process. Though several research outputs have shown that the increase of catalyst content increases the amount of desired fuel like liquid products, there is an optimal range. The conversion efficiency even decreases after the optimal range of catalyst to waste plastic ratio based on the type of catalysts, plastics, and reaction temperature [12]. Acidity of the catalysts governs the quantity of the desired liquid yield. Highly acidic active catalysts can lead to further cracking of the liquid hydrocarbon in the reaction chamber resulting into more gaseous products and coke [12].

Generally the cracking of HDPE produces more linear n-paraffins. But the presence of linear paraffins in diesel fuel causes gelled suspension in normal temperature. As a result, it requires isomerization to produce branched isomers so that both the cloud point and the freezing point of the fuel can be lowered with the reduction of formation of wax crystals [40]. Catalytic dewaxing [36] of the yield fuels can be considered one of the effective methods to overcome these issues along with lowering the boiling range (T95). This process also retains the cetane rating of the diesel fuel derived from plastics. The catalysts are preferably of large pore sizes and higher silica (e.g. Beta-zeolite/high silica Y) based or ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-35 and ZSM-38 for dewaxing isomerization. On the other hand, selective paraffin isomerization dewaxing [1] can be implemented with the catalysts like aluminosilicate zeolite to improve the fuel quality by handling only the linear n-paraffin. Thus the available highly branched-isomers, aromatic and cycloaliphatic compounds in the derived fuel are not affected by the catalyst.

Many studies on catalytic conversion of different types of plastic polymers to different products including chemicals and fuels, using different type of catalysts have been published [41]. The most widely used are Zeolite base catalysts such as ZSM-5 [42], silica, alumina [43], basic catalysts, such as BaCO₃ [44], Bimetallic catalyst Al-Zn composite [45], and FCC catalyst [46]. Despite the fact that most of these catalysts worked in terms of plastic waste conversion, still they are associated with either high cost of production or the operating condition may not be industrially feasible as high temperature and more residence time with low percentage conversion might be the case. Highly acidic behavior of the catalysts reduces the liquid yields but lighter hydrocarbons of gasoline categories [47]. Table 3 presents several more thermo-catalytic degradation processes and their yield compositions. It has been shown that the problem occurred in the pyrolysis process only with the PVC, PS and mixed plastics can be resolved by using appropriate solvent/light gas cleaner, e. g. NaHCO₃ + AgNO₃ mixed solution in a some appropriate quantity. The conversion rate of fuel standard liquid has been observed more than 50 wt% consisting of carbon chain length C3-C32.

Researchers [5, 35, 48, and 49] reported that the content of aromatic hydrocarbons may be small or even very small for non-catalyzed pyrolysis but in the presence of catalysts (particularly zeolites) they observed an increase in the amount of aromatic hydrocarbons in the liquid. Strongly acidic catalysts like HZSM-5 zeolites yield lighter hydrocarbons (C3-C6), whereas, the less acidic catalysts like microporous HMCM-41 can produce heavier hydrocarbons from conversion of waste plastics [36]. Manos et al. [37] observed that the order of catalysts' activity on HDPE could be presented as, (lighter hydrocarbons) ZSM-5 < mordenite < β < Y < US-Y (heavier hydrocarbons) and (alkenes dominant) ZSM-5 < mordenite < β < Y < US-Y (alkanes dominant). Choosing an appropriate catalyst for the particular plastic to obtain transport fuel is a key factor to successful accomplishment of the process.

Though, catalysts may decrease the temperature of the process, change the selectivity and the composition of the products, they give more gas product, the catalysts are quickly deactivated and recovering and regeneration of them is not easy. It may increase the costs of the process. Many researchers and inventors have proposed fluidized-bed reactors due to their advantages, i.e. difficulties with the mixing of the wastes, removing of the coke, regeneration of the catalyst, and heat transfer resistance may be solved and/or reduced in an easy way. However, the fluidized-bed reactors may be profitable probably only in large industrial-scale plants due to the investment costs [56].

The catalytic process followed by the thermal liquefaction of plastics with various catalysts can reduce the problems associated with the disintegration of the plastic wastes, wall to plastic particle heat transfer issues, sticking of the cracking raw materials with the reactor walls, cooking of reactor walls, etc. which are found in the thermal conversions only [56].

Table 3. Waste plastic to fuel conversion processes in presence of various catalysts

Type of Mixture	Plastic	Process	Temperature	Pressure	Catalysts	Time (min)	Solvent/light gas cleaner	% Fuel Yield	Remarks
Mixed Plastic [50]	50 gm PS + 25 gm PVC	Thermo-catalytic degradation (TCD)	200-430 °C		5 wt% ZnO	201	0.5(N) NaHCO ₃ + 0.2 (N) AgNO ₃	50.08% (C3-C32) (0.86gm/ml)	Cl content is high in PVC that is left as residue. Electricity

									Consumption 0.433KWh
Mixed Plastic [51]	50% waste plastics (LDPE, HDPE, PP, PS mixture) + 50% tire	Thermo- catalytic degradation (TCD)	250 - 430 °C		2 wt% Fe ₂ (CO ₃) ₃	270	0.5(N) NaOH + 0.25(N) NaHCO ₃ + 0.25(N) AgNO ₃	47.4% (C3-C20) (0.78 gm/ml)	Higher residue (37.7%) due to other contents in tire and PS that cannot be converted into fuel. Electricity Consumption 0.711 KWh
Mixed Plastic [52]	LDPE, HDPE, PP, PS mixture	Thermo- catalytic degradation (TCD)	200 - 400 °C		20 wt% ZnO	258	0.25(N) NaHCO ₃ + 0.25(N) AgNO ₃	87.19% (C3-C36) (0.77 gm/ml)	Plastics were cut into pieces of 2-3mm size. Electricity Consumption 6.25 KWh
[38]Homoge- neous	HDPE	Catalytic degradation	400 °C (Heating rate of approximatel y 20°Cmin ⁻¹)		CAT1 (7% SO ₃) and CAT2 (3.5%SO ₃) modified Zirconium catalysts (Calcined @ 550 °C for 3hrs then cooled down in desiccator before using.)			34.31% oil + 65.68% gas (with CAT1), and 53% oil + 46.98% gas (with CAT2)	Fixed-bed reactor. The sizes of the plastic and catalysts were 125-150µ and 75-100µ respectively. Oil composition with CAT1 is more of aromatic type which is favorable with gasoline. The oil yielded by CAT2 is olifinic (65%) which is good for industrial uses.
[1]Homoge- neous	LDPE	Catalytic Pyrolysis	175-400 °C	Atm. Pressure	1g (20 wt%) CaC ₂	60		69.73% fuel oil + 30.07% gas + 0.2%char	Batch reactor, Optimal liquid yield was found at 350 °C
Mixed Plastic [53]	24 wt.% HDPE + 39 wt.% LDPE + 21.5 wt.% IPP + 10 wt.% PS + 4 wt.% ABS + 1.5 wt.% PET	Thermo- catalytic decompo- sition	420-440 °C (For HZSM- 5), and 450- 480 °C (For PZSM-5),	Atm. Pressure	HZSM-5 and orthophos- phoric acid modified (PZSM-5) zeolite catalysts	120		52 wt% liquid (with HZSM-5), and 47.33 wt% liquid (with PZSM- 5)	Extruder type fixed bed reactor. Thermocatalyti c process produces lighter olefins and paraffins along with increased alkyl aromatics.
[54] Mixed Plastic	PS and HDPE	catalytic degradation	400 °C (heating rate 9 °C/min)	Atm. Pressure, N ₂ stream	Catalyst: Reactant (1:10). Spent	38, 49			Semi-batch reactor (stirring speed of

			(20 cc/min)	FCC catalyst.		200 rpm).
[16]Homogeneous	Waste Polypropylene	Catalytic pyrolysis	400 °C to 550 °C (10°C/min) Batch reactor made of stainless steel (SS) tube	Kaolin clay (SiO ₂ 43.12%, Al ₂ O ₃ 46.07%, Fe ₂ O ₃ nil, MgO 0.027%, CaO 0.030%, ZnO 0.0064%, K ₂ O 0.01%, TiO ₂ 0.74) catalyst to plastics ratio (1:2, 1:3, 1:4, 1:6, 1:10, 1:20, 1:40)	87.5 wt% liquid (745 kg/m ³ , 2.18 Cst) + 11.75 wt% gaseous + 0.75 wt% residue	The highest yield of oil (87.5wt.%) was obtained at the ratio of plastics to catalyst 3:1 at 500°C. The catalysts could be reused for several times and reduces the activity after 4 times of re-using due to deposition of carbon and wastes over the catalyst's surface.
[55]Homogeneous	LLDPE	catalytic degradation		20% and 40% ultrastable Y zeolite (US-Y)	N ₂ gas (50 ml/min) in order to remove the volatile yields	Semi-batch Pyrex reactor. containing only a small amount of zeolite, cracking catalysts are less acidic and produce, therefore, more liquid hydrocarbons than their parent zeolite
[28]	HDPE	Catalytic cracking	381 °C - 427 °C	Al ₂ O ₃ (HDPE:Catalyst = 7:1)	N ₂ gas	Conversion efficiency 65.4% (89.6% liquid + 10.4% wax). Semi-batch reactor with about 50% efficient electric heating system.
[56]	Polyolefins (HDPE, PP)	The melting and cracking process (Clementi Process) in tubular reactor with the molten metal bed called "the tube in the tube"	419 °C – 428 °C	Alloy based molten metal bed (59-61 wt% of Tin + 38-4 wt% of Lead + 1wt% of Impurities) of 8.5 g/cm ³ and melting temperature of 183-185 °C		93.31 wt% liquid (~10 mol% light wax, and ~50 wt% light gasoline) + 6.69 wt% gaseous hydrocarbons No solid residue was found at the end of the conversion process. Products can be treated to produce transport grade fuel or directly used in electricity generation.

							The content of aromatic hydrocarbons in liquid yield is lower than other reactors.
[57]	LDPE film	Catalytic Pyrolysis	550 °C (10 °C min ⁻¹)	NiMo/Al ₂ O ₃ (2.72 wt% Ni + 13.16 wt% Mo + 84.12 wt% Al ₂ O ₃). Plastic to catalyst ratio = 20:1	The reactor was completely purged with dry nitrogen to remove air.	Conversion efficiency is 93.8%. (85.3 wt% liquid + 8.5 wt% gaseous + 6.2 wt% solid residue), liquid fraction's heating value is 10,810 Cal/g, which is higher than that of fuel oil.	Batch reactor. Though the pyrolysis occurs in absence of oxygen, the presence of catalyst reduces the degradation temperature and increases the fraction of liquid yield.

4. Discussion

Every nation in the world, especially the highly populated as well as the developed countries, has been facing the continuous accretion of the plastic wastes in the garbage dumping places. Also, both the landfilling and incineration based waste dumping have been pushing the earth toward the environment saving challenges. Various types of diseases are now observed due to environmental pollution caused by these polymer wastes.

Pyrolysis (thermal cracking) process of waste plastics alone has been facing few obstacles to produce fuels according to the fuel standards. Thermal liquefaction in presence of hydrogen gas pressure system can produce more liquefied hydrocarbons than the nitrogen based thermal cracking system.

The catalytic cracking followed by the thermal liquefaction can facilitate the effective conversion of waste plastics into liquid fuel. Only catalytic process faces the obstacles with mixed and dirty plastics as the catalysts are mixed before the degradation starts. That causes production of more chars and wide ranges of hydrocarbons. But when the waste plastics are liquefied in presence of hydrogen and then the catalysts are introduced in the yield of this process, the combined process provides better process efficiency. Also the consumption of catalysts is optimized with this mixed mechanism. Moreover, the problem with the mixed plastics is resolved in this thermo-catalytic process.

Thermo-catalytic process can reduce the process temperature of the thermal cracking process alone. The liquefied and the gaseous hydrocarbons from the liquefaction process can be easily mixed with the catalysts. Therefore, the less catalyst consumption reduces the process expenditure. Besides, the problem with the PVC, PS type plastics can be resolved in the thermo-catalytic process with an optimal solution of NaOH, NaHCO₃, and AgNO₃. As a result, most of the unprocessed waste plastics can be fed into the thermal liquefaction chamber for fuel production purpose.

5. Conclusion

Various types of catalysts have been found effective in converting the plastics into desired fuel category products. Among them the Kaolin clay (SiO₂ 43.12%, Al₂O₃ 46.07%, Fe₂O₃ nil, MgO 0.027%, CaO 0.030%, Zn), Silica-Alumina, Zeolites (beta, USY, ZSM-5, REY, clinoptilolite, etc.), and MCM-41, etc. are the frequently used catalysts. In case of de-chlorination purposes, some light gas cleaners are used in optimal way based on the plastic category. Therefore, the aromatic content and the corrosive contents are reduced. With the catalytic integration, the overall process temperature is reduced. So, the thermo-catalytic process can be industrially or nationally sponsored

to reduce solid polymer wastes from environment. Alternative fuel production can effectively reduce the fuel import load of any nation producing more plastic wastes.

Acknowledgements

Acknowledgements and Reference heading should be left justified, bold, with the first letter capitalized but have no numbers. Text below continues as normal.

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