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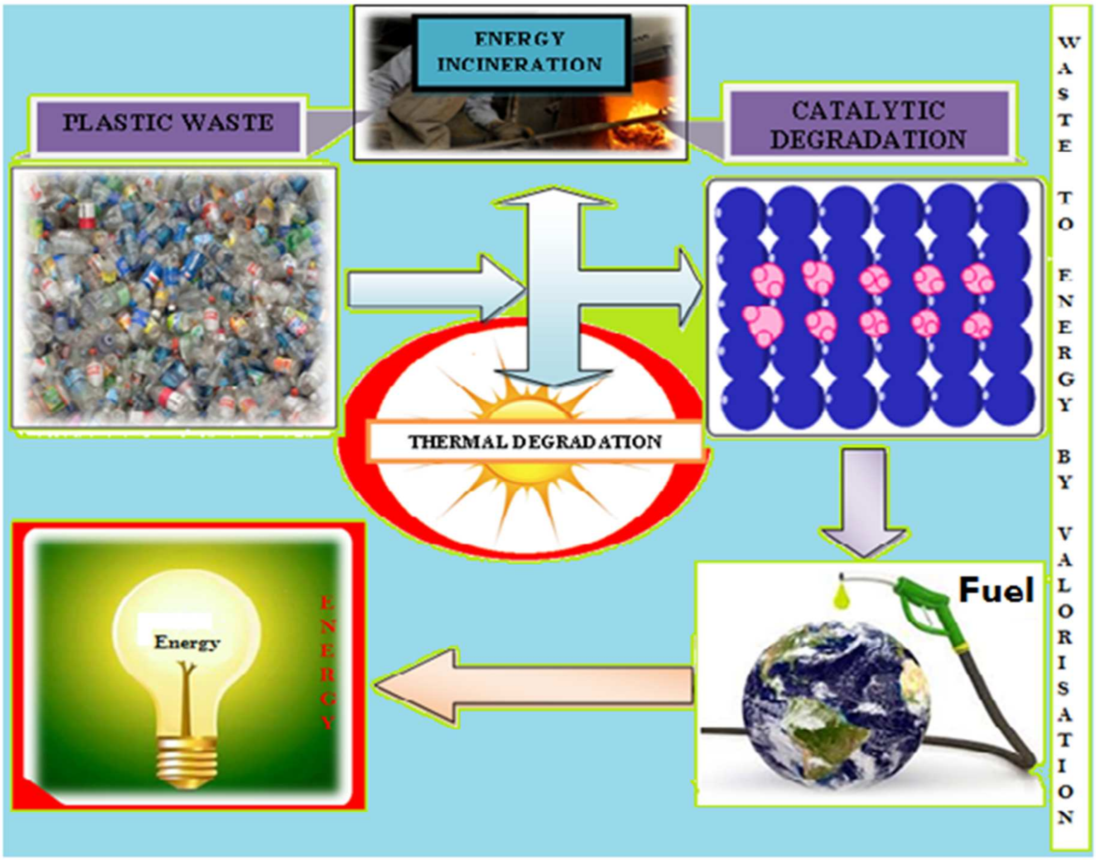

Waste to energy: Catalytic degradation of plastic waste can provide valuable energy carriers

Heterogeneously catalyzed strategies for the deconstruction of high density polyethylene: plastic waste valorisation to fuels

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ABSTRACT

The plastic industry generates enormous quantities of plastics at projected rates (both production and consumption) which can significantly threaten our environment in terms of plastic waste generation. High density polyethylene (HDPE) is one of the main fractions of municipal solid waste which has a remarkable potential to be valorised into fuels (e.g. bio-oils). Catalytic degradation is an innovative alternative process to transform plastic waste into such value added products. This mini review is aimed to discuss the most relevant and recent catalysts developed for the catalytic degradation of HDPE including metal oxides, sulphated metal oxides, zeolites, nanostructured zeolites, molecular sieves, fluid catalytic cracking (FCC) catalysts, metal carbonates and mesoporous materials for the production of chemicals and fuels (e.g. diesel and gasolines). Activities and selectivities as well as important effects of additives, particle size, catalyst to polymer ratios and also recent approaches for waste management will be discussed.

1. Introduction

The major production of plastics in current society is based on petrol-derived feedstocks. Plastics production accounts for over 280 million tonnes (Mt) in 2011, a 4% increase with respect to 2010.[1] From 2010 to 2016, global plastic consumption is expected to continuously grow in similar yearly numbers to those previous stated.[1] The continuous production and use of plastics however leads to a significant generation of plastic waste due to their inherent non-degradable nature, with over 24.9 Mt plastic waste produced only in EU-27, Norway and Switzerland in 2008.[2] Packaging accounted for the most important contribution to plastic waste generation (> 60%).[2]

Current options to manage plastic waste are generally limited to recycling and incineration (with or without energy recovery) as well as landfill disposal. These basic waste management practices were able to drive a total recovery (energy recovery and recycling) to over 50% of plastic waste, with ca. 21% of recycling rate.[2] What is more important, practices including incineration generate in some cases hazardous emissions of potentially carcinogenic compounds (e.g. polychlorinated dioxins and polychlorinated furans) as well as poisonous gases such as phosgene. Comparatively, plastic recycling based on pelletizing and moulding to low grade plastics have attracted the interest of many scientists worldwide, but the recycled plastic possess poor mechanical strength and color qualities, hence having low market values and restricted applications.

These figures and inherent issues of plastic recycling clearly evidence the need to seek alternative advanced sustainable valorisation practices able to provide technologies for the production of high added value products from plastic waste including chemicals and fuels. Plastic recycling which includes conversion of waste plastics into valuable chemicals and fuels has attracted a significant interest worldwide.[3-7] Plastic depolymerisation strategies to monomers or relatively higher complexity units could offer a promising alternative to plastic recycling.[8] Nevertheless, complete plastic depolymerization into monomers is only possible in restricted cases and generally never exceed 95-97% (e.g. monomer recovery for polymethyl methacrylate (PMAA) is high, close to 97%, while for polystyrene is just about 70%).[9] Plastic waste valorisation can also be approached by thermal degradation methods. However, these protocols generally involve high temperatures (>500°C) and generate a wide product distribution.[10, 11]

In the light of these premises, it is clear that the conversion of plastic waste into fuels and valuable chemicals can only be approached in a sustainable way by means of catalytic degradation techniques. Suitable catalysts and reactor design can in principle be potentially able to control product yield, product distribution as well as to reduce reaction temperature. As example, vinyl polymers (e.g. polyethylene and polypropylene) are very difficult to decompose to their monomers because of random C-C bond fission of polymer chain during the reaction mechanism which generates a broad range of products, when decomposed at high temperatures.[12, 13] Catalytic degradation of such plastics can yield much narrower product distribution of carbon number and also reduces reaction temperature thus offering a more environmentally sound approach which can potentially lead to more cost effective processes for a range of valuable products.

There are various types of polymers discarded every year in large quantities from which high density polyethylene has a low tendency towards degradation. The decomposition properties of waste plastic follows the order depicted in Figure 1.

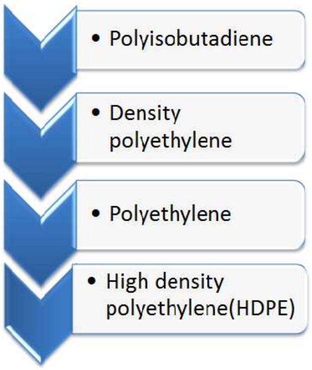


Figure 1. Decomposition of a series of waste plastics

HDPE is part of the polyolefins family and one of the main polymers in municipal solid waste, [14, 15] being very rich in carbon and hydrogen. Its H/C ratio is closer to that of petroleum.[16] HDPE volume in 2007 accounted for 23% (ca. 5 million tons) of Western Europe's total polyolefins production, which represents at the same time close to 40% of total plastic production in Europe.[17] Obviously, these significant numbers illustrate the high volumes of discarded HDPE annually only in Europe.

This contribution has been aimed to discuss strategies and possibilities in the deconstruction of HDPE to valuable fuels (e.g. diesel, bio-oils) using a series of heterogeneously catalyzed protocols.

2. Catalytic degradation of HDPE

2.1 Seminal studies and key processes

Conversion of waste plastics/coal mixtures into valuable hydrocarbon fuels requires the use of different catalysts.[18-20] These waste plastics can be converted into bio-oils either via pyrolysis of plastics using acid catalysts or by direct liquefaction of plastics in the presence of acid catalysts.[21-28] Higher average molecular weight and less branched HDPE is comparably more difficult to degrade with respect to other resins, while low density polyethylene (LDPE) is relatively easy to degrade to gaseous or liquid fuel products.[29-40]

The detailed thermal depolymerization mechanism of linear HDPE was originally proposed by Holmstrom in 1976. The mechanism involves a radical chain mechanism, showing two possible termination reactions as depicted in Figure 2.[41]

2.2. Catalysts employed in HDPE catalytic degradation

2.2.1 Zeolites

Several reports followed from such seminal work, mostly related to the utilisation of zeolites as solid acids for HDPE catalytic degradation. These include investigations on the use of clinoptilolite or fluid catalytic cracking (FCC) catalysts (''fresh'' or ''used''). Clinoptillolite (natural zeolite) catalysts usually have pore structure of monoclinic framework consisting of a 10-membered ring (7.6×3.0 Å) and an 8-membered ring (3.3×4.6Å).

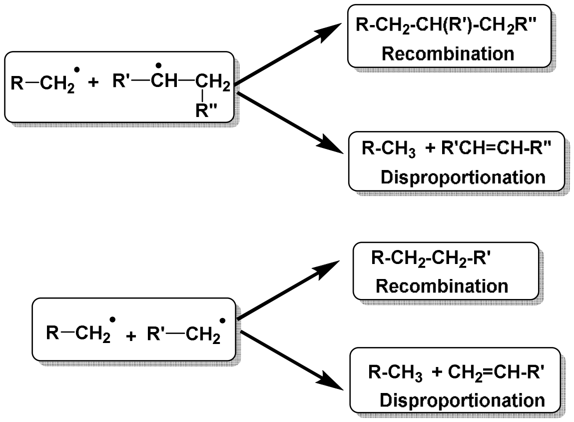


Figure 2. Holmstrom proposed radical chain mechanism for thermal depolymerization of linear HDPE.

Clinoptillolite is a silica-rich member of the heulandites family as compared to ZSM-5 catalyst which contains pores of relatively small size (about 5×5 Å).[42] HZSM-5 was initially reported to be useful for HDPE depolymerization using tetralin as solvent,[43] followed by a combination with $TiCl_3$ in both tubing and autoclave reactors.[44] Pyrolysis of high-density polyethylene (HDPE) using a specially developed laboratory fluidized-bed reactor operated isothermally at ambient pressure was proved to produce valuable hydrocarbons in the range of C_3-C_5 carbon number with a high olefinic content.[44] The addition of $TiCl_3$ or HZSM-5 was found to have a significant effect on solid yields (i.e. char) which remarkably decreased as compared to those of conventional thermal runs. As example to illustrate such important effect, solid yields were reduced to ca. 3% for catalytic runs with respect to a staggering 44.8% for non-catalytic runs at 430 °C.[44] No significant non-catalytic reactions were found to take place below 430 °C. The chemistry behind the process encompassed HZSM-5 catalyzed cyclization and aromatization reactions as well as $TiCl_3$ catalyzed recombination and disproportionation reactions. Optimum oil yields (88.7%) were obtained for HDPE catalysed depolymerisation using $TiCl_3$, while maximum gas yields of 21.2% were observed, when HZSM-5 was employed as catalyst in the autoclave reactor under the investigated reaction conditions.[44]

Further studies on the catalytic degradation of HDPE indicated that catalysts such as ultrastable zeolite–Y (USY) possessed a profound effect in reducing catalytic degradation temperatures in semi-batch reactors as compared to purely thermal non-catalytic degradation.[45] USY is a microporous zeolite containing supercages (12 Å) tetrahedrally connected by 12-membered ring windows of 7.4 Å diameter. The particle size of the reported catalyst was 1µm. Gel permeation chromatographic studies in fact confirmed that solid state reactions occurred in presence of the microporous catalyst. As the system reached to its final temperature, the reaction rate for the formation of volatile products decreased rapidly. C_3-C_{15} range products were observed in the liquid fraction, being isobutene and isopentane the main gaseous products (Table 1).[45]

Alkene-rich liquid products were also obtained which underwent a series of bimolecular transfer hydrogenation reactions to give *iso*-paraffins as major products. These compounds have associated high octane numbers which illustrate the potential of catalytic degradation in terms of commercial technology for plastic waste valorisation. The observed selectivity to the liquid fraction (ca. 50%) was interestingly found to be insensitive to temperature.

On a separate study, USY zeolite was also employed as catalyst in the catalytic decomposition of both LDPE and HDPE under dynamic conditions in a batch reactor.[46] The particle size of the investigated catalyst was 1µm. Interestingly, no appreciable differences could be observed in terms of product distribution among the gaseous products formed by both LDPE and HDPE. Aromatic compounds were obtained from 440 ºC to the end of the catalytic decomposition process.[46]

Table 1. Liquid product distribution of the catalytic degradation of high-density polyethylene at various experimental conditions (heating rate and final temperature)

	Mass fraction of liquid (%)			
Conditions	Alkanes	Alkenes	Cycloproducts	Aromatics
100 K/min to 649K	73	7	4	16
100 K/min to 570K	75	5	3	17
100 K/min to 529K	83	2	4	11
2 K/min to 559K	86	3	3	8

The catalytic activities of various aforementioned zeolites including FCC, HZSM-5 and clinoptilolite were compared by Miskolczi and co-workers for the catalytic degradation of plastic waste (HDPE and polystyrene) in batch reactors.[47] HZSM-5 was proved to significantly increase the yield of gaseous products due to its higher microporous surface area as compared to clinoptillolite, in good agreement with previous reports.[43, 44] In any case, both FCC and natural clinoptillolite catalysts exhibited good catalytic activities for the production of light hydrocarbon liquids comprising C_5-C_{28} compounds of various types including linear non-branched structures (mostly *n*-paraffins and alkenes) with some aromatics (e.g. ethyl-benzene, styrene, toluene, and benzene). Product variability was dependent upon cracking parameters and an interesting difference in yield to products was observed between crushed and uncrushed catalysts, particularly for FCC and ZSM-5 catalysts (Figure 3).[47]

Nano-sized crystals of HZSM-5 can be more active for external cracking processes to generate molecules small enough to pass through the pores to further undergo over cracking to increase the gas yields. In some cases, a poor contact between catalyst and plastic residue reduces the gas production.[48-50]

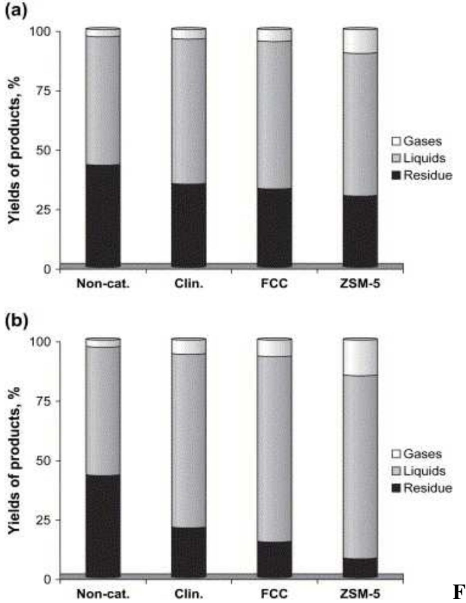


Figure 3. Yields of products (a) over uncrushed and (b) crushed catalysts at 430 °C. Reprinted with permission from Ref. 47. Copyright 2013 Elsevier Ltd.

HDPE was thus catalytically degraded under these reaction conditions over nanocrystalline H-ZSM-5 (crystal size ~100 nm) to produce improved gas yields between 350-550 °C. Of note was the higher yield of butenes (25%) in the gas fractions under the investigated conditions. Waxes obtained in the catalytic degradation comprised linear and branched paraffins, in the C_{10} to C_{20} range. Either an increase in the polymer to catalyst ratio or keeping operation temperatures below 450 °C had an associated detrimental effect in gas generation in the systems.[51] Interestingly, catalytic degradation at temperatures over 500 °C pointed to significant changes on gas and liquid compositions due to the thermal degradation of HDPE, increasing the olefin concentration in the waxes. A plausible mechanism was suggested in which polyethylene was cracked to waxes on external surface acid sites of the zeolite which then further diffused into the internal active surface sites and overcrack to produce lighter compounds.[51] Intensive and strong external acid sites of nanocrystalline H-ZSM-5 lead to the remarkable advantages to promote higher yields of gaseous fractions and to provide a higher selectivity to desired products.[49, 51]

Zeolite acidity is one of the key influencing factors in catalytic degradation studies. Coelho and co-workers studied the influence of ZSM-5 zeolite acidity on catalytic degradation of HDPE using simultaneous DSC/TG analysis.[52] For degradation of HDPE, both pure HDPE and a mixture of HDPE with catalysts were placed in an alumina TG pan and experiments were conducted to find out the temperature for maximum HDPE degradation rates (Table 3).[52]

Table 2. Degradation temperature for the HDPE/zeolite samples obtained from TGA/DSC analysis.[52]

Sample	T_{degrad} (°C)
HDPE	483.2
HDPE+ NaHZSM-5 (80)	465.1
HDPE+ NaHZSM-5 (63)	413.1
HDPE+ NaHZSM-5 (50)	405.7
HDPE+ HZSM-5	402.2

Notably, (80), (63) and (50) are three different NaHZSM-5 zeolites obtained by a single exchange with a 0.5M $NaNO_3$ solution, with a single exchange with 1.0 M $NaNO_3$ solution and by two successive exchanges with 1.0 M solutions, respectively.

Fairly similar results were obtained for most zeolite catalysts, although increasing acidity (Si/Al 50 ratio in NaHZSM-5 (50) could reduce degradation temperatures from 465.1 to 405.7 ºC, similar to those of H-ZSM-5 (Table 2, last entry).

Comparably, nanocrystalline beta zeolites were developed as an efficient solid acid catalyst for the degradation of HDPE in the liquid phase.[53] As previously mentioned, zeolites with smaller crystallite sizes have been regarded as better catalysts for plastic waste degradation providing large external surface areas and high acidity required for the initial cracking step. For this purpose, six different beta zeolite catalysts having different Si/Al ratios or crystallite sizes were synthesized[53] and used for HDPE degradation in a round bottom flask, purged with nitrogen. The reaction temperature was set at 380 °C to avoid thermal degradation of HDPE favoured at temperatures above 400 °C. Nanocrystalline H-beta zeolite with crystallite size around 10 nm and low Si/Al ratio (high acidic) was found to be an efficient catalyst for the degradation of HDPE in liquid phase. Liquid products were collected in a burette through condenser maintained at -4 °C and the amount of gaseous products was determined by measuring continuously the product flow using a

Ritter TG05 gas flow meter. Liquid product yields were found to be ca. 80%, with high selectivities to C_7-C_{12} hydrocarbons.[53]

2.2.2 Silicates and metal oxides

Functionalised silica and silico-alumino-phosphates were found as alternative to zeolite materials, FCC catalysts and gallosilicates for plastic waste valorisation. LDPE could be converted to valuable compounds using an H-gallosilicate as catalyst.[54] Valuable aromatic hydrocarbons, mainly benzene, toluene and xylenes (BTX) could be produced in the protocol which in principle was suggested to be easily converted to polypropylene and mixtures thereof.[55] In fact, later studies from the same group demonstrated that the HDPE catalytic degradation over the gallosilicate yielded lighter hydrocarbon mixtures rich in valuable aromatic components.

Fluidized bed systems are capable of a better isothermal control and mass transfer. Powdered catalysts, namely silica-alumina (SA) and silica-alumina-Na_2O (denoted as F9) have been employed by Luo *et al.* for the HDPE in a fluidized bed system.[56] In terms of textural properties, both (F9 and SA) catalysts were similar except a higher specific surface area with a smaller pore volume of F9 catalyst. The authors found that SA exhibited a better catalytic activity producing higher yields of liquid fuels and more valuable gas products under a temperature range between 400-550 °C.[53]

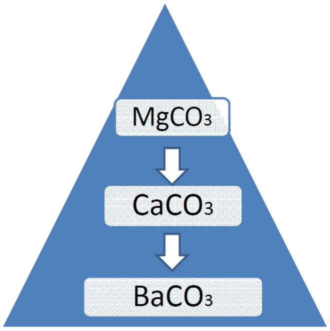
Various zeolites including HZSM-5, H-Y, H-beta, SAPO-37, AlMCM-41 and Al-TUD-1 have been utilised for the degradation of polyethylene (PE and/or HDPE) in recent years.[57-77] SAPO-37, belonging to the class of silicoaluminophosphates, was prepared using a hydrothermal approach by Fernandes and co-workers[65] for HDPE degradation. Silicoaluminophosphate (SAPO) molecular sieves represent an important class of materials generated by the introduction of silicon into its aluminophosphate framework.[55] According to thermogravimetric analysis and Vyazovkin model-free kinetic method, the activation energy required for HDPE degradation in the absence of catalyst decreased from 290 to 220 kJ mol^{-1} for SAPO-37/HDPE. It was also found to be selective for the decomposition of HDPE into light hydrocarbons (C_2-C_{12}).[56]

Pyrolysis of HDPE resulted into higher yields of gaseous products (up to 95%)[77] at temperature between 500 to 800 °C with respect to a combined gas and oil yield of 52 wt. % achieved via catalytic degradation of HDPE over a silica-alumina catalyst (catalyst/sample ratio = 1:1, 320 °C, within 60 min).[78] A significant temperature reduction in the catalytic valorisation of HDPE could provide superior yields to products. Moreover, an 80 wt.% liquid yield could be obtained using sulphated zirconia at temperatures ranging between 420-450 °C with high initial H_2 pressures (500-2000 psi) for 0.5-3.0 h reaction time.[79] Other catalysts with additional metal element supported on sulphated zirconia, including $Ni/ZrO_2/SO_4^{2-}$ and $Pt/ZrO_2/SO_4^{2-}$, could even maximize bio-oil conversion to 99 wt.% with 19-30 wt.% gas yield at 375 °C.[80] The addition of a large volume of catalyst provided large yields of gaseous products.

Another important parameter influencing the thermal degradation of HDPE is the effect of additives.[81-82] In principle, additives, including $Al(OH)_3.xH_2O$, $AlC1_3$, $CaCO_3$, Al_2O_3, CuO, Fe_2O_3 and ZrO_2, are thermally stable below 600 °C except $Al(OH)_3.xH_2O$ and $AlC1_3$. Findings pointed out that large quantities of gaseous products were obtained in the presence of zirconia at 460 °C, while oil production (up to 80%) was maximized under analogous conditions using calcium carbonate.[83] Several interesting results were disclosed related to the advantage of catalytic HDPE degradation as compared to non-catalytic degradation which generally does not take place in relevant quantities to products at temperatures under 490 °C.

2.2.3 Other catalysts

Basic catalysts are particularly relevant materials for the conversion of HDPE waste to fuel oil. Jan *et al.* proved the use of magnesium carbonate to be effective for "waste to fuel" transformation under batch mode operational conditions. HDPE bottles were cut into 5-10 mm^2 sized pieces and utilised as feed for the degradation process. An increase in the formation of gaseous products was observed at 400 °C while no conversion was observed at 250 °C. Temperature was increased in intervals up to 450 °C, with only wax and gaseous product formation maximised at temperature between 410-420 °C (no yields of liquids). A further increase in temperature favours the formation of liquid products, with a maximum conversion to the liquid fraction observed at 450 °C. Obtained liquid fractions comprise high quantities of C_8-C_9, C_{13}-C_{14} and C_{17}-C_{18} hydrocarbons. According to distillation data, nearly 50% of the liquid fraction has boiling point in the range of gasoline while the remaining 50% was in the diesel oil range.[84] The degradation of waste HDPE into fuel products using $BaCO_3$ under batch conditions was also reported.[85] Optimum conditions for the formation of oil were similar to those above mentioned for $MgCO_3$ catalytic degradation. $BaCO_3$ was found to be slightly higher selective for oil generation as compared to $MgCO_3$. Similarly, product selectivity using $CaCO_3$ was inferior to that of $MgCO_3$ under the same reaction conditions.[85] Catalysts were found to follow the selectivity order (for oil production):



More recently, Ahmad *et al.* reported HDPE cracking at 350 °C under nitrogen in the presence of mild acidic nano-structured $BaTiO_3$ catalysts.[86] $BaTiO_3$, $Pb/BaTiO_3$, $Co/BaTiO_3$ and Pb-$Co/BaTiO_3$ were prepared via reactive calcination and well characterized by XRD, SEM, EDX and SAA.[86] The hydrocarbon range product distribution changes for each type of nanomaterial as compared to a blank run (without catalyst) as clearly evidenced in Table 3.

Table 3. Catalytic effect of various $BaTiO_3$ nanomaterials on hydrocarbon range products in HDPE-derived liquid fractions.[86]

Catalyst[a]	Distribution of hydrocarbon range products (%)				
	C_6-C_{12}	C_{13}-C_{16}	C_{17}-C_{20}	C_{20}-C_{30}	$\geq C_{30}$
No catalyst	32.56	30.80	14.19	12.35	10.95
$BaTiO_3$	15.45	33.83	16.71	24.38	8.05
$Pb/BaTiO_3$	17.91	27.45	19.64	31.49	3.49
$Co/ BaTiO_3$	24.34	35.45	22.42	13.05	4.4
Pb-$Co/BaTiO_3$	18.55	31.34	25.71	16.02	7.88

[a] Catalyst loading : 1%

C6 to C16 products comprised over 62% of total selectivity under purely thermal conditions. Comparatively, the addition of catalysts generally provided a shift towards longer C chain products C13 to C30 (Table 3), mostly alkanes as indicated in Table 4. Hydrocarbon distribution also showed reduced naphthalenes and olefins yields after doping with Pb and/or Co which points to a preferential catalytic activity towards hydrogen transfer reactions.[86]

Table 4. Effect of individual catalyst on hydrocarbon group types in liquid fractions derived from HDPE.[86]

Catalyst[a]	Product distribution (%)			
	Olefins	Naphthalenes	Alkanes	Aromatics
No catalyst	31.90	8.40	59.70	0.0
$BaTiO_3$	32.17	2.22	65.61	0.0
$Pb/BaTiO_3$	22.5	4.14	73.36	0.0
$Co/ BaTiO_3$	19.92	3.2	76.89	0.0
$Pb\text{-}Co/BaTiO_3$	24.64	4.38	70.73	0.0

[a]Catalyst loading: 1%

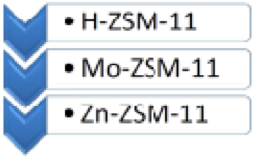
The use of FCC spent catalysts has also been considered as a candidate to plastic waste degradation, particularly for the liquid-phase catalytic degradation of waste HDPE and polystyrene (PS) mixtures in a semi-batch reactor at 400 °C.[87] Different mixing proportions of reactants possessed an important effect on the final characteristics of the obtained liquid products. Increasing PS content from 0 to 100 wt.% produced larger quantities of gasoline fraction (from ca. 85 to ca. 98 wt%). Additionally, PS addition was also found to accelerate the production of aromatic components, showing the highest selectivity (> 60 wt.%) for ethyl benzene and styrene.[87]

2.2.4 Catalyst comparison: microporous vs mesoporous materials

Much attention has been paid to mesoporous zeolites in past years due to their improved performance in catalysed reactions with respect to conventional (purely microporous) zeolites.[88] Zeolites (e.g. zeolite-Y, ZSM-5) are indeed conventional fluid catalytic cracking (FCC) catalysts but generally zeolite-type materials have inherent mass transport issues related to their rather small porous structure. For further reading on processes to overcome such issues (e.g. mesoporosity development in zeolites), readers are kindly referred to the outstanding contributions of the group of Perez-Ramirez.[88] Particularly related to HDPE pyrolysis, MCM-type mesoporous materials (2-20 nm pore size range) were compared to zeolite-Y, alumina and HZSM-5 in terms of catalytic performance. Al-containing MCM-41 was found to have similar degradation rates to those of HZSM-5 in HDPE degradation, confirming the potential of mesoporous materials in plastic waste valorisation.[89]

Pyrolysis of HDPE has also been similarly reported using laboratory fluidized-bed reactor isothermally at ambient pressure over various catalysts using HZSM-5 as compared to non zeolitic catalysts including MCM-41 and SiO_2-Al_2O_3 (SAHA) and mixtures zeolite/MCM and zeolite/SAHA. Degradation over HZSM-5 resulted in much larger amounts of volatile hydrocarbons as compared to those observed using non-zeolitic catalysts. SAHA and MCM-41 materials facilitate bulky reactions to occur, leading to the generation of coke and subsequently deactivation of the catalyst. Yields of volatile hydrocarbons using such catalysts followed the order (HZSM-5>MCM-41/HZSM-5>SAHA/HZSM-5). The highest product yield (nearly 94 wt.%) was obtained for HZSM-5. A higher BTX formation was also observed using HZSM-5.[90]

Microporous and mesoporous materials, namely ZSM-11 and a modified MCM-41 as a mesoporous material were also compared in terms of efficiency and product distribution in the degradation of HDPE.[57] Zn, Mo and H-ZSM-11 materials were found to be selective for liquid hydrocarbon (LHC) production, namely benzene, toluene and xylenes (BTX). Zn-zeolite exhibited the highest levels of LHC (>57 wt.%), with a BTX selectivity of 47 wt.%. Comparatively, H-zeolite produced a higher fraction of gaseous hydrocarbons (C_1–C_4) to those observed for Mo- and Zn-zeolites. In contrast, Zn-MCM-41 produced mainly C_5–C_{16} products. Complete conversion of HDPE could be achieved in the temperature range of 410-500 °C. LPG (C_3–C_4) levels were also interesting for all materials, following the order:



A more recent study focused on hierarchical MFI zeolites for the liquid phase degradation of polyethylene.[91] In this work, HDPE, LDPE and LLDPE were converted into useful fuels. MFI zeolites provide large surface area by dividing into small zeolite moieties which promotes a good contact between the polymeric material and the catalyst. Partial dissolution of the zeolite framework by alkali generated target mesopores in zeolite crystals[92-94] which seemed to play an important role in the degradation process together with the skeletal structure of the polyethylene.[71, 95, 96] Four types of mesoporous MFI zeolites, namely MFI-sda, MFI-alk, MFI-oxy and MFI (nano, commercial) were prepared. The optimum HDPE conversion (>95%) was reported for MFI-sda at 380 °C. MFI-sda exhibited highly ordered mesopores and strong acidic sites so that even low catalyst loadings (HDPE/catalyst = 20 g/0.05 g) at 380 °C was found to be sufficient to provide high conversion in the systems (95%).[91] In general, MFI zeolites were found suitable for HDPE degradation, providing high external surface areas and a rapid mass transfer.

3. Latest trends

Continuous pyrolysis coupled with catalytic cracking

Conical spouted bed reactors (CSBR) have been reported to provide a good performance in continuous pyrolysis of HDPE for the production of waxes. A two-step system combining thermal and catalytic cracking of HDPE (Figure 4) involves CSBR pyrolysis followed by catalytic cracking using zeolites in a fixed bed reactor. This combination was found to be useful for the conversion of HDPE to waxes (first step) and waxes to olefins (second step) as depicted in Figure 4.

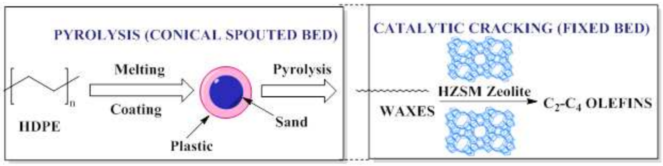


Figure 4. Two-step thermal and catalytic process for HDPE cracking. Adapted from reference number [97]

HDPE was converted into olefins using the proposed two-step methodology using HZSM-5 zeolites with different acidity. In this investigation, three different HZSM-5 catalysts were prepared with various SiO_2/Al_2O_3 ratios (Table 5). HZSM-5 with a SiO_2/Al_2O_3 ratio of 30 provided a high yield (58 wt.%) of light olefins and propylene (32 wt.%), which in any case were rather similar to those obtained in a single stage HDPE catalytic cracking process at the same temperature significantly higher catalyst loadings (ca. almost 4 times, Table 5).[98]

Table 5. Comparison of olefin and propylene yield obtained in single step and two-step process.[98]

Process	SiO_2/Al_2O_3 ratio	Light olefin yield (wt%)	Propylene yield (wt%)
Catalytic process (Single-Step)[a]	30	57.0	28.0
	80	59.8	29.0
Pyrolysis + catalytic cracking (two-step)[b]	30	58.0	32.0
	80	43.6	24.1
	280	35.5	18.8

Operating Conditions: [a] 500°C, 30 g_{cat} min g_{HDPE}^{-1}; [b] 500°C + 500°C, 8 g_{cat} min g_{HDPE}^{-1}

Catalytic co-processing studies of binary mixtures of plastic and biomass waste using thermogravimetric analysis have also been recently reported.[99] A comparison study of catalytic and non-catalytic co-processing of rubber seed shell (RSS) and HDPE mixtures using thermogravimetric analysis indicated that activation energies (E_A) and pre-exponential factor (A) values for binary mixtures are comparatively lower to those of pure HDPE but comparable to pure RSS.[99] These results may pave the way to a future utilisation of plastic waste/biomass mixtures for catalytic valorisation of HDPE.

Similar to HDPE, plastic grocery bags are responsible of relevant environmental concerns which include the ever increasing concentration of plastic waste in the pacific,[100-102] lethal to animal health and society.[103-105]

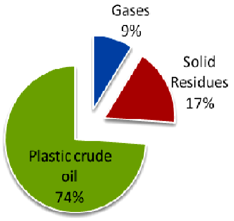


Figure 5. Product yields from plastic grocery bags. Adapted from reference number[106]

Sharma et al. recently studied the thermo chemical conversion of plastic grocery bags (HDPE) under batch conditions (Figure 5).[106a] In a typical process, pyrolysis of HDPE waste grocery bags was followed by distillation resulted into a hydrocarbon mixture. Upon analysis of the obtained hydrocarbons, the mixture was found to contain primarily saturated aliphatic paraffinic compounds with a similar boiling point range to that of conventional petroleum diesel fuel.

Corn derived plastic bags have been also pyrolyzed to bio-oils under microwave-assisted irradiation.[106b] Bio-oil upgrading can subsequently lead to high quality hydrocarbon fuels with important advantages in terms of storage, transportation and implementation in current fuel infrastructure.[107-108]

4. Incineration energy recovery

Waste-to-energy technologies were recently discovered and re-invented, emerging as potentially useful protocols to create renewable energy from waste matter, including municipal solid waste (MSW), industrial waste, agricultural waste, and waste byproducts.[109] Valorisation of plastic waste is prioritised as compared to agricultural waste due of their inherent previously discussed environmental issues and non- disposable nature. Another promising and important area for plastic waste valorisation relates to energy recovery from incineration of municipal solid waste (MSW). This has been accomplished in many developed countries since several decades ago in an effort to approach sustainable development.[110-113] Incineration-based technologies yield high volume of recoverable energy which is comparable (if not superior) to those obtained with other technologies i.e. anaerobic digestion.

Figure 6 shows a general process flow of a typical refuse-derived fuel (RDF) plant aimed to convert mixed municipal waste into energy. Four main processing steps associated with RDF process include physical separation of incombustible materials, drying of MSW, size reduction and pelletizing.

In recent years, life cycle assessment,[114] 3R (reduce, reuse and recycle) methodologies, [115] tertiary recycling[116] and plasma pyrolysis and pyrolysis technology[117] are protocols for HDPE conversion to energy are among the most promising alternatives for future waste plastic waste management from MSW. Energetic recovery from polymers currently has promising future prospects to tackle plastic-related environmental problems.[116]

5. Conclusions and future prospects

This contribution has been aimed to highlight some of the key developments for the design and preparation of heterogeneous catalysts for waste plastics conversion to fuel oil. A number of catalytic systems have been reported in this regard which have been investigated to better understand their effects on fuels production and product/chemical distribution. Some of these effects (e.g. for zeolite-based catalysts, solid basis, mesoporous materials, etc.) have been discussed and illustrated in plastic degradation studies in terms of conversion and selectivity. Reported findings addressed (1) the use of fluidized bed systems which provide enhanced mass transfer and thermal homogeneity for catalysts and reactants mixtures, (2) certain structures in nano-sized zeolite crystals which possessed unique high conversion and selectivity to produce fuel oil from plastic waste, (3) the effects of additives on plastics waste conversion and (4) the effects of porous systems (micropores vs mesopores) in the framework of the proposed "waste to oil" concept.

To date, ideal "waste to oil" transformation processes are a great challenge because they require high reaction temperatures and difficulties to control conversion as well as selectivity to the different products, particularly for plastic waste. Lowering the reaction temperature is always a long-term goal in catalytic processes which can in principle made possible by the appropriate design of advanced catalytic materials. Catalyst design, with a particular focus on active phases (*benign by design* nanomaterials) and porous networks, can undoubtedly pave the way to increasingly efficient protocols for plastic waste conversion. Future efforts should be geared towards enhanced and more controllable low-temperature processes using alternative technologies (e.g. microwave irradiation, continuous flow systems) able to provide energy-saving, scalable and tunable process to maximise plastic waste conversion as well as target selectivities (e.g. diesel or gasoline fractions).

The authors of this contribution sincerely hope the future can bring more sustainable advances in the field for an environmentally sound processing of waste plastics to valuable products including fuels and chemicals.

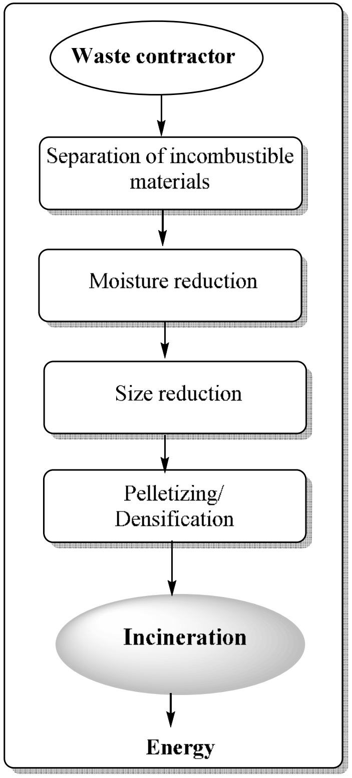


Figure 6. Process flow of a conventional RDF plant

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Biographies

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Dr. Manoj B. Gawande received his Ph.D. degree in Chemistry in 2008 from the Department of Chemistry, Institute of Chemical Technology (formerly UDCT), Matunga, Mumbai, India, with Prof. R.V. Jayaram. During his research tenure, he has been awarded several prestigious fellowships, including Brain Korea-21 (BK-21) Research Fellowship from the Ministry of Science, South Korea and FCT Research Fellowship from MCTES, Lisbon, Portugal. After several research stints in Germany, South Korea and Portugal, he worked as a Visiting Professor at CBC-SPMS, Nanyang Technological University, Singapore and visiting scientist at the Department of Chemistry, Cambridge University, Cambridge, UK with Prof. Steve Ley. Presently, he is working as a Senior Researcher and Head of the Nanocatalysis and Organic Synthesis Research laboratories at the Regional Centre of Advanced Technologies and Materials, Faculty of Science, Palacky University, Olomouc, Czech Republic. His research interests include nanocatalysis, magnetically recyclable nanomaterials and their applications in organic transformations. He has published over 50 scientific publications, including reviews, patents and articles. He is currently supervising several doctoral and postdoctoral students.

Rafael Luque (Ph.D 2005 from Universidad de Cordoba, Spain) has a significant experience on biomass and waste valorisation practises to materials, fuels and chemicals as well as nanoscale chemistry and microwave and flow chemistry. He has published over 220 research articles, filed 3 patent applications and edited 7 books as well as numerous contributions to book chapters and invited, guest, keynote and plenary lectures in scientific events worldwide. He is also heavily involved in Chemical Education and promoting Science in Developing Countries. Among recent awards, Rafael has received the Marie Curie Prize from Instituto Andaluz de Quimica Fina in Spain (2011), the Green Talents award from the Federal Ministry of Education and Research in Germany (2011), the TR35 Spain from Technology Review and MIT (2012) and the RSC Environment, Sustainability and Energy Early Career Award (2013) from the Royal Society of Chemistry. Rafael has also been recently honored as 2013 Distinguished Engineering Fellow and Visiting Professor from CBME at Hong Kong University of Science and Technology in Hong Kong and currently Chinese Academy of Sciences Visiting Professor at the State Key Laboratory of Electroanalytical Chemistry of the Changchun Institute of Applied Chemistry. Prof. Luque combines his academic duties with his activities as young entrepreneur after co-founding Green Applied Solutions S.L.U. and more recently taking part of Posidonia Oceanica S.L. in Spain.

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