

# CATALYSTS FOR THE CONVERSION OF WASTE PLASTICS: CHALLENGES FOR THE DEVELOPMENT OF INDUSTRIAL PROCESSES

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## Abstract

*The utilization of plastics has been increasing and subsequently the volume of domestic and industrial waste plastics (municipal, production and e-waste) has been increasing significantly. The phenomenal growth of IT industry and exorbitant use of plastics demands environmentally friendly solutions for recycling of waste plastics into value added materials and effective recovery of non-renewable materials from the waste plastics. Novel and hybrid catalytic materials and processes are the need of the hour to address the challenges for waste plastics (individual/commingled) conversion and upgradation processes. The catalytic materials should address the value addition to the waste plastic streams, avoid the environmental damage (soil, air, water) from the non-biodegradable plastics due to toxic/corrosive halogenated components added to the plastics.*

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**Keywords:** waste plastics, catalysts, fuels, halogenated compounds, recycling

## 1. Introduction

Worldwide plastic industry witnessed a steady growth in recent years, which reflected in the increased consumption of all types of plastic materials. World-wide, the plastics and polymer consumption will have an average growth rate of 5% and may touch a figure of 227 million tons by 2015.

In today's modern world, plastics make a fundamental contribution to all activities such as agriculture, automobile industry, electricity and electronics, building materials, packing and so on. This is primarily because of the substitution of other materials with plastics as well as their applications in new areas, and material's durability and versatility. The share of plastics in e-waste and municipal waste has seen a phenomenal increase in the recent years. The rapid growth in plastics consumption is increasing and subsequently plastic waste is accumulated, and poses serious problems to the environment due to their non-biodegradable nature.

Recovery can be classified as material recycling (mechanical and feedstock) and energy recovery (gasification and combustion). Mechanical recycling is limited solely on single polymer thermoplastic waste and not applicable to thermosets. Incineration of plastic waste to produce heat may be a possibility, but its organic content would totally be destroyed and converted into green house gas (CO<sub>2</sub>) and H<sub>2</sub>O. Due to the world's limited reserves of coal, crude oil and natural gases it becomes very urgent to preserve the existing non-renewable materials and to find other carbon sources (biomass) as feedstock materials or as fuels.

Pyrolysis is one of the best methods to recover the material and energy from polymer waste, as only about ca. 10% of the energy content of the waste plastic is used to convert the scrap into valuable hydrocarbons. This is obtained by breaking down polymers at high temperatures into petrochemical feedstock components from which they originate. The main drawback to thermal degradation is the requisite high temperatures (process is highly endothermic) that results in a very broad range of products [1], which requires severe reaction conditions and produces low value products. Hence, the role of catalysts and catalytic process are immense importance in producing very high value hydrocarbons from the waste plastics in an environment friendly manner.

## 2. Catalysts for Plastics Pyrolysis

Catalysis is an interdisciplinary science and technology. Catalysis is an integral component in any green processing technology, serving as an important tool to support sustainable development. Sustainable development is essential to deal with the challenges of a fast changing world, where demands on natural resources, the needs of a growing population and the accumulation of waste will inevitably impose restriction upon how business operate. Where a manufacturing process is energy intensive, a controlled recycle/reuse is an effective means of decreasing overall negative environmental impacts [2].

The catalytic reactions take place in the solid-gas or solid-liquid interface. The amazingly wide range of chemical transformations in petroleum refining is based mainly on two types of catalytic transformation: hydrodehydrogenation and acidic hydrocarbon catalysis. The first type controls the distribution of hydrogen among

hydrocarbon products while the second type, the acid catalyst, controls the carbon number and boiling range, the skeletal structure as well as the types of hydrocarbons produced. Today's advanced catalysts combine these two catalytic functions with highly specific catalyst structure features, called shape selectivity, which control the size and other chemical features of molecules produced.

The deployment of catalysts ensures lower operating temperatures and/or pressures and a higher selectivity to the target product with a resultant reduction in fuel usage and waste production. A catalytic approach to waste polymer reprocessing has the following positive features: (a) lower operating temperatures (relative to pyrolysis), non-oxidative process with lower energy requirements and no directly associated NO<sub>x</sub>/SO<sub>x</sub> emissions; faster reaction rate; selectivity increased towards similar type of compounds; (b) absence of thermally-induced free radical reactions that can lead to toxic intermediates; (c) possibility of selective Cl & Br removal (in the case of Chlorine and Bromine containing polymers) with concomitant polymer degradation to a target recyclable product; (d) operability in a closed system with no toxic emissions etc..

Plastics can be divided into two groups: (i) condensation polymers; (ii) addition polymers (polyolefins). Condensation polymers, which include such materials as polyamides, polyesters and nylon can be "depolymerised" via reversible synthesis to the starting diacids and diols or diamines. The solid catalysts (existing and newly developed) can provide solutions to the first class of polymers (polyolefins) for effective conversion. The novel and hybrid solvents has to be developed for the depolymerization (for monomers and oligomers) of condensation polymers. In both these cases the presence of additives and new combinations will create the complications for the development of catalysts and solvents.

Waste from Electrical and Electronic Equipment (WEEE) contains plastics and metals in it. In 2009, India generated approximately 330,000 tonnes of e-waste. E-waste contains hazardous (lead, mercury, cadmium etc..) and precious material (gold, silver, copper etc..). An average PC approximately weighing 31.5 kg contains 7.24 kg of plastics, 1.98 kg of Pb, 0.693 g of Hg, 0.409 g of As, 2.961 g of Cd, 1.98 g of Cr, 9.92 g of Ba, 4.94 g of Be. In about 315 million computers about 550 X 10<sup>6</sup> kg of Pb, 900 000 kg of Cd, 180 000 kg of Hg and 0.5 X 10<sup>6</sup> kg of Cr IV are present. It also has 1800 X 10<sup>6</sup> kg of plastic and at least 159 X 10<sup>6</sup> kg of brominated flame retardants from monitors [3]. With this present situation, the development of new catalysts, reactors, and processes are highly desirable to address this important issue.

### 3. Present Status

There has been a plethora of research work in the conversion of waste plastics into fuels and chemicals. The fundamental investigations and mechanistic investigations of thermal decomposition of polymers have been published by Madorsky [4]. Kaminsky et al [5] reported that the plastic waste and tires can be converted

into fuels and chemicals [5]. The initial catalytic cracking research primarily focused on polyolefin feedstocks because these polymers are the most abundant in plastic waste [1-18]. In one of the first polymer catalytic cracking studies using the noble metals on silica-alumina, Uemichi and co-workers reported the use of silica alumina, activated carbon, Pt/silica-alumina, and Pt/alumina catalysts for poly(ethylene) (PE) cracking [6]. Ayame et al [7] produced the branched polyethylene by catalytic degradation-isomerization of high density polyethylene (HDPE) using silica-alumina catalyst. The comparative studies with the acidic and non-acidic catalysts and mesoporous materials [17] have been studied to show the effect of acidity on the cracking of polyolefins [12, 14-15]. In the mixed waste streams, the halogenated plastics cannot be avoided and poses several problems in the thermal and catalytic pyrolysis in the presence of various catalysts [4-18]. Dehydrochlorination of plastic mixtures was studied by Bockhorn [18] and others [19-23] to provide the base for understanding the decomposition mechanism of PVC containing mixed plastic waste, which has become the base for the development of catalyst/sorbents for the production of halogen free hydrocarbons from the commingled waste plastics. Yoshioka et al. [20] showed the mechanistic pathways for the two stage decomposition of PVC and PVDC plastics for the effective dehalogenation of PVC mixed plastics into halogen free hydrocarbons [21] and Kamo et al described the effect of pressure on the degradation of PVC [22]. We have shown that the effect of HIPS-Br (e-waste plastic) in the mixed streams on the products distribution and dehalogenation processes with the carbon composite catalysts [24-25]. Serrano et al [26] showed the effectiveness of new generation catalysts such as hierarchical zeolites for the pyrolysis of plastics. Various above mentioned catalysts have been used for the commercial processes for the conversion of waste plastics with certain limitations. Due to the limitations and economics, the alternatives for the costly catalytic materials has been looked by various groups and Fujimoto et al [27] developed and utilized the disposable catalysts (spent FCC) for the commercial processes.

### 4. Challenges

Catalysts are a class of compounds specially selected, designed and optimized for influencing the reaction mechanism, subsequently the high-value products. Catalyst activity, selectivity, and stability are major considerations. Theoretically, waste plastics have excellent fuel value, quite comparable to that of gas oil, when only polyolefins are considered. Introducing hetero-atoms, such as oxygen, nitrogen, or chlorine, reduces the heating value. The major hetero-atoms appearing in polymers are: oxygen, nitrogen, chlorine, bromine, fluorine. After plastics pyrolysis, these elements either appear as intermediate organic compounds still incorporating the hetero-element, or as stable inorganic compounds, i.e. water, ammonia and hydrogen cyanide, hydrogen chloride, hydrogen bromide and bromine,

hydrogen fluoride. Most of these are hazardous and corrosive components require a careful selection of catalysts/sorbents for their effective removal/processing, as well as methods to neutralize or inhibit their effect.

A major problem in pyrolysis is in the rather unpredictable specifications of both feedstocks (diffusion/steric hindrances of bulky molecules), if it is a mix of plastics, and products. Hydrogenating conditions lead to the elimination of hetero-atoms and yield more saturated products as well, an important consideration regarding the marketing of pyrolysis products.

Little is known on the effect of fillers or coke precursors (styrene, butadiene etc.) on catalytic activity and catalyst fouling, coking, or clogging. Another area of interest is the effect of catalyst addition on the thermal decomposition in the liquid phase. It seems unlikely that the macromolecules can contact the internal catalyst surface in a productive fashion. Some additives may also influence the product distribution by modifying the cracking mechanism and hence, product distribution. Regeneration and life of the activity of catalysts is an issue. Development of low cost materials for the specific targeted production (light olefins, aromatics) from the waste plastics is highly desirable.

Robust and stable catalytic materials for the effective conversion of halogenated mixed plastic waste to produce valuable hydrocarbons while recovering the valuable halogen content. The non-renewable and very precious metals present in the e-waste should be processed to recover both fractions (metallic and plastics). The energy efficient and environment friendly methods for the closed loop systems and materials for the waste plastics conversion to avoid any waste (residue) are highly desirable and challenging. The other typical problems and possible solutions in industrial case studies will be discussed during the presentation.

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