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NPTEL ONLINE
CERTIFICATION COURSE

WASTE TO ENERGY CONVERSION

ENERGY PRODUCTION FROM WASTE PLASTICS-1

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Plastics and their classification

Plastic is a material consisting of any of a wide range of synthetic or semi-synthetic organic compounds that are malleable and can be molded into solid objects.

Plastics are typically organic polymers of high molecular mass, but they often contain other substances like fillers, plasticisers and colourants.

- Fillers improve performance and/or reduce production costs.
- Plasticizers are oily compounds that confer improved rheology.
- Colourants are common additives, although their weight contribution is small.

**** Some of the additives can be toxic**

Plastics are commonly derived from petrochemicals, but many are partially natural.

There are two types of plastics: **thermoplastics and thermosetting**.

Thermoplastics do not undergo chemical change in their composition when heated and can be molded again and again. Thermosets can melt and take shape once; after they have solidified, they stay solid.

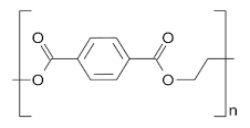
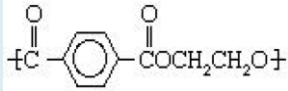
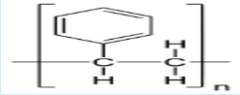


Plastics recycling and SPI code

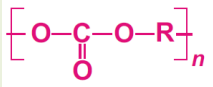
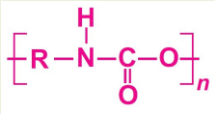
http://www.ryedale.gov.uk/attachments/article/690/Different_plastic_polymer_types.pdf

Type & code		Typical Examples	
PET		Beverage bottles, medicine jars, rope, clothing and carpet fibre	
HDPE		containers for milk, motor oil, shampoos and conditioners, soap bottles, detergents, and bleaches	
PVC		All kinds of pipes and tiles, commonly found in plumbing pipes.	
LDPE		cling-film, sandwich bags, squeezable bottles, and plastic grocery bags	
PP		Lunch boxes, margarine containers, yogurt pots, syrup bottles, prescription bottles, plastic bottle caps etc.,	
PS		Disposable coffee cups, plastic food boxes, plastic cutlery and packing foam	
Others		Polycarbonate, ABS, Nylon, Polylactide	

Different types of plastics and their monomers

Name(s)	Formula	Monomer
Polyethylene low density (LDPE)	$-(CH_2-CH_2)_n-$	ethylene $CH_2=CH_2$
Polyethylene high density (HDPE)	$-(CH_2-CH_2)_n-$	ethylene $CH_2=CH_2$
Polypropylene (PP)	$-[CH_2-CH(CH_3)]_n-$	propylene $CH_2=CHCH_3$
Poly(vinyl chloride) (PVC)	$-(CH_2-CHCl)_n-$	vinyl chloride $CH_2=CHCl$
PET/ PETP	$(C_{10}H_8O_4)_n$ 	bis(2-hydroxyethyl) terephthalate 
Polystyrene (PS)	$(C_8H_8)_n$ 	Styrene $C_6H_5CH=CH_2$

Different types of plastics and their monomers

Name(s)	Formula	Monomer
Polycarbonate		Organic functional groups linked together by carbonate groups
Acrylonitrile butadiene styrene (ABS)	$(C_8H_8)_x \cdot (C_4H_6)_y \cdot (C_3H_3N)_z$	Acrylonitrile, butadiene, styrene
Nylon 66	$(C_{12}H_{22}N_2O_2)_n$	HOOC-(CH ₂) ₄ -COOH (Adipic acid), hexamethylene diamine H ₂ N-(CH ₂) ₆ -NH ₂
Polyurethane (PUR and PU)		<u>organic</u> units joined by <u>carbamate</u> (urethane) links (mostly thermosetting)

Suitability of plastic types for energy production

Type(s)	Thermo-Fuel System Suitability
Poly-ethylene(PE)	Very good
Poly-propylene(PP)	Very good
Poly-styrene(PS)	Very good(gives excellent fuel properties)
ABS resin(ABS)	Good. Requires off-gas counter measure
Poly-vinyl chloride(PVC)	Not suitable, should be avoided
Polyurethane(PUR)	Not suitable, should be avoided
Fiber Reinforced Plastics(FRP)	Fair. Pre-treatment required to remove fibers.
PET	Not suitable, should be avoided

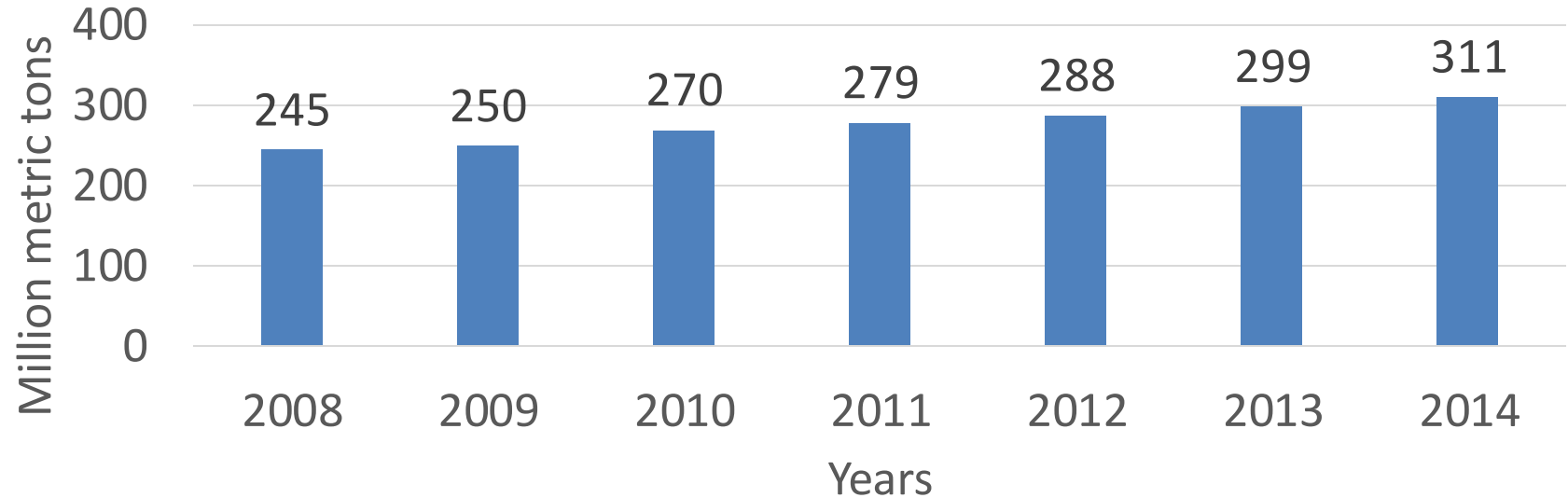


Plastic wastes generation and its need for proper management

Source : <http://www.statista.com/>

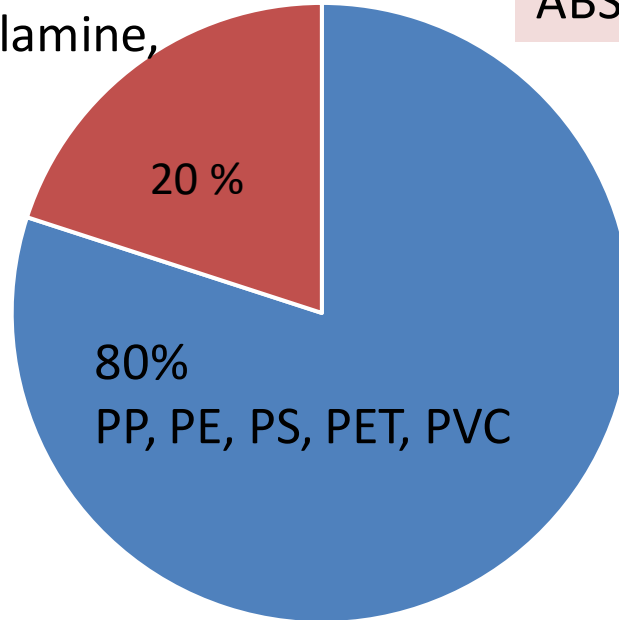
- In 2008, world annual production was 245 million metric tons which increased to 311 million metric tons in 2014.

Annual production of plastics



Plastic waste generation in India and its composition

ABS, PC, Malamine,
Thermocol



PC: Polycarbonate

ABS: Acrylonitrile Butadiene Styrene

- ▣ 120 thousand TPD of MSW is generated in India
- ▣ 10 thousand tons per day (TPD) of plastics waste in our country, which is ~ 9 % of MSW

<http://www.cpcb.nic.in/139-144.pdf>

Plastic wastes generation and its need for proper management

In India waste plastics form widespread littering on the landscape due to the lack of proper management techniques

Around eight million tons of plastic wastes are dumped in the ocean each year.

The plastics are not bio-degradable

In spite of the above facts, due to user friendly nature (lightweight, durability, energy efficiency etc.), ban of plastics could not succeed in India.

Recycling and reuse of waste plastics is highly necessary

Pyrolysis is a cost effective process and is applied for waste tyre management and being investigated for using waste plastics.



Options for management of plastics wastes

❑ Recycling

- Primary recycling – Product characteristics similar to those of original product.
- Secondary recycling – Product characteristics different from those of original plastics product.
- Tertiary recycling - Production of basic chemicals and fuels from plastics waste/scrap as part of the municipal waste stream or as a segregated waste.
- Quaternary recycling - Retrieves the energy content of waste/scrap plastics by burning / incineration. **This process is not in use in India.**

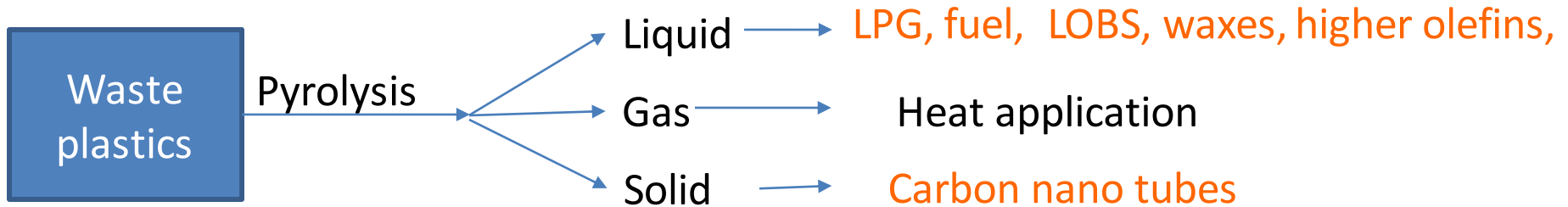
CPCB recommended options

- Polymer coated bitumen for road
- Plasma gasification
- **Liquid fuel production**

Recycling of waste plastics through pyrolysis

(Present scenario)

- ▣ PE & PP can be thermally /catalytically degraded to produce liquid and gaseous hydrocarbons
- ▣ For valorification, waste PE & PP can be converted to various value added products like LPG, fuel, LOBS, waxes, higher olefins, carbon nano tubes etc with emphasis for the end products that have good market.
- ▣ Number of processes have been developed world wide. However, most of them produce a liquid product - a sort of plastic crude.
- ▣ Some small and medium scale plants are operative in India and other countries, but these do not have wide acceptability



Yield Calculation

In a laboratory, a 50g of waste plastic sample is pyrolyzed in a batch reactor (weight=750g). Weight of collected oil is 37g and final weight of reactor is 755g. Calculate the yield of gas, liquid and solid fractions.

$$\text{Liquid(wt\%)} = \frac{\text{Weight of liquid}}{\text{Weight of feed}} \times 100$$

$$\text{Solid(wt\%)} = \frac{\text{Weight of solid}}{\text{Weight of feed}} \times 100$$

Mass balance:

$$\text{Gases(wt\%)} = 100 - (\text{Liquid(wt\%)} + \text{Residue(wt\%)})$$

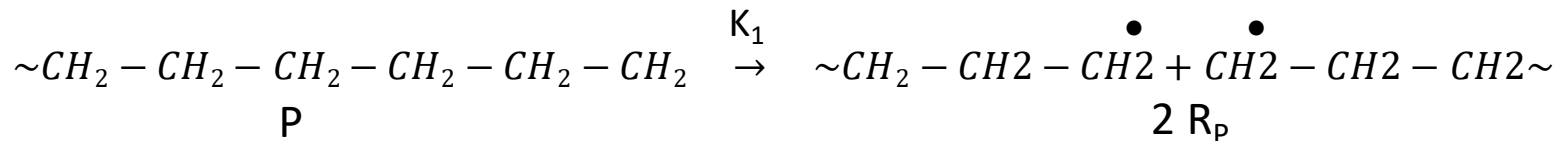
$$\text{weight of solid} = 755 - 750 = 5\text{gm.}$$

$$L = 74\%, S = 10\%, G = 16\%$$

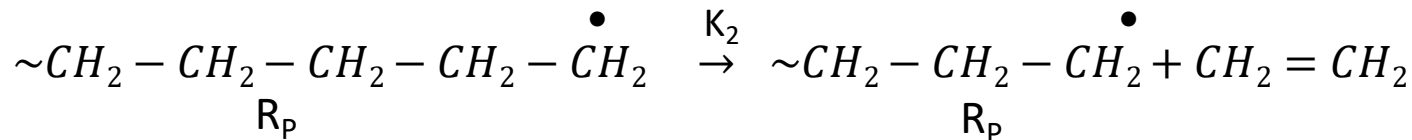


Reaction Mechanism

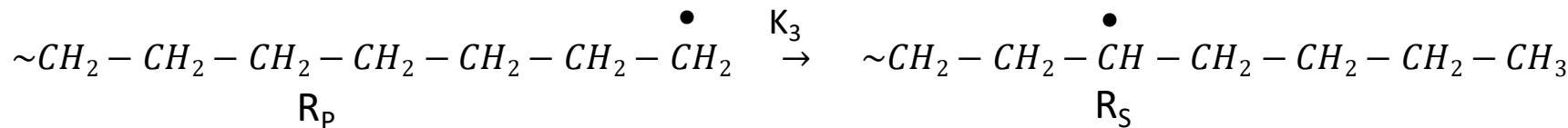
Initiation:



Propagation:



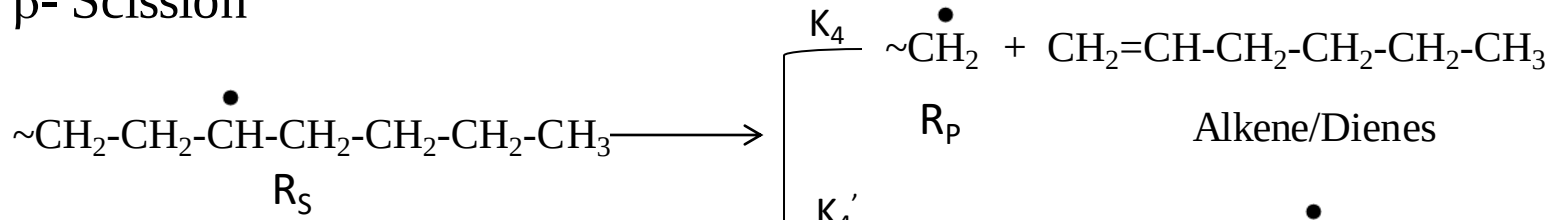
Hydrogen transfer, intramolecular



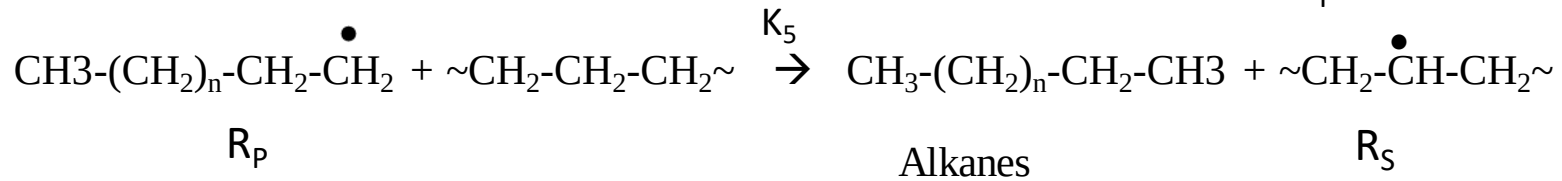
Source: Feedstock Recycling of Plastic Wastes by José Aguado, David P. Serrano [Scheme 4.1]

Reaction Mechanism

β - Scission



Hydrogen transfer, intermolecular



Termination (2nd order) : Recombination



Pyrolysis Processes

1. Thermal Pyrolysis

- Process involves operation at high temperatures(350-900°C).
- Formation of liquid products have wide distribution of carbon number.

2. Catalytic pyrolysis

- Process reduces reaction temperature and reaction time.
- The quality of liquid product obtained is better.
- It helps to narrow down the product distribution of carbon number to gasoline and diesel range.



Pyrolysis of plastic depends on mainly

- ✓ Plastic type and blend
- ✓ Temperature
- ✓ Residence time
- ✓ Presence of catalyst
- ✓ Catalyst loading
- ✓ Catalyst contact mode
- ✓ Reactor Type

Batch Mode,
Continuous Flow Mode,
Fixed Bed,
Fluidized Bed Reactor etc.

Product yield at 425 °C from real waste plastics (German source) in batch reactor

Product(s)	Thermal Pyrolysis	Cat. Pyrolysis (zeolite)
Oil	~76.7 %	~81.4 %
Gas	~7.3 %	~9.6 %
(char & CaO)	~16 %	~9 %

Catalyst presence enhanced the yield of both gas and oil products and reduced the yield of char product.

Source:

N. Insura, J. Onwudili and P. T. Williams, University of Leeds

<https://www.researchgate.net/file.PostFileLoader.html?id=54940deccf57d7d8228b4657&assetKey=AS%3A273655018262540%401442255848468>

Catalytic Pyrolysis

- When catalysts are utilized in pyrolysis, two kinds of decomposition mechanisms works simultaneously:
 - Thermal cracking : Random chain scission, scission the end of chain and elimination of side groups(free radical mechanism).
 - Catalytic cracking : Carbenium ions adsorbed on surface, beta scission and desorption.
- The catalyst can promote:
 - Increased process selectivity.
 - Decomposition reactions at low temperature with lower energy consumption.
 - Reduced costs.
 - Liquid products with a lower boiling point range.



Catalytic Pyrolysis

- Heterogeneous catalysts have been more used due to their easy recovery.
- The homogenous catalysts used are Lewis acids like AlCl_3 , FeCl_3 .
- The heterogeneous catalysts: solid acids, zeolites, silica alumina & and FCC cat.
- The acidity of their active sites and crystalline microporous structure favor hydrogen transfer reactions and thereby make them suitable for obtaining high conversion at low T.
- Differences in the catalytic activity of these solids are related to their acidic properties, especially the strength and number of acidic sites.
- The properties of structures, as the particle size, pore size distribution and specific area have a crucial role in their performance.



Common steps for converting waste plastics to fuels

- ✓ Collection & segregation
- ✓ Storing of plastics waste
- ✓ Shredding of wastes
- ✓ Feeding into hopper
- ✓ Flow of waste into heating vessel in presence or absence of catalyst
- ✓ Movement of liquid-vapor into condenser
- ✓ Collection of liquid fuel (as a product)

Thanks...

