

## Catalytic Pyrolysis of General Purpose PolyStyrene Using Red Mud as a Catalyst

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### Abstract

*In this work, the influence of Red Mud in the pyrolysis of general purpose polystyrene (GPPS) has been studied. The catalytic pyrolysis experiments were carried out using an unstirred semi-batch stainless steel 6.28 liter reactor under nitrogen atmosphere (air free) with Red Mud as a catalyst. The reaction effluents (oil and gases) were condensed in water-cooled condenser. The condensate was weighted to determine the total yield. Gas Chromatography-Mass Spectroscopy (GC-MS) analysis was used to characterize the condensed liquid organic compounds. According to the GC-MS results, styrene, benzene and its derivatives, toluene, naphthalene and a small amount of the other hydrocarbon compounds were identified in condensate liquid. Density, specific gravity, API gravity, kinematics and dynamic viscosity, flash point, fire point, cloud point and pour point of condensate were also measured. Under optimum reaction condition, the yield of pyrolysis reaction was above 90%. The air free reaction condition showed good catalytic pyrolysis of polystyrene with less than 1% coke formation and above 90% selectivity towards formation of aromatic compounds. The specifications of condensate, i.e. density, API gravity, viscosity and flash point observed showed that the liquid obtained can safely be classed as a kerosene. The specific gravity value was close to the specific gravity value of diesel.*

**Keywords:** Waste Polystyrene, Catalytic Pyrolysis, Red Mud

### 1. Introduction

Used general purpose polystyrene (GPPS) from household and industries is recognized to be a major environmental problem. There are several methods for disposal of municipal and industrial GPPS wastes, i.e. landfill, incineration, true material recycling, and chemical recovery. Landfill treatment and destruction by incineration are quite expensive and pose serious air pollution problems due to the release of airborne

particles and carbon dioxide into the atmosphere [1].

The net cost of disposal can be effectively reduced by true materials recycling where waste materials are converted into a reused one. But GPPS is a class of waste materials that true materials recycling can't be applied as a long term remedy to the GPPS waste management. Chemical recycling is widely accepted as a proper alternative to the true materials recycling worldwide. In chemical recycling, plastic wastes were converted into fuel oil and valuable chemicals [2–6].

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Pyrolysis is an effective chemical recycling method. It has been employed to convert waste plastic into useful products such as fine chemicals, transportation fuels, and lubricant oils. Pyrolysis is also classified as the chemical and energy recovery system known as cracking, gasification and chemolysis methods.

In the pyrolysis process (heating in an oxygen free atmosphere), the materials (containing organic components) with higher molecular weights are decomposed, generating liquid and gaseous products that can be used as a fuel and/or as sources of raw chemicals. The inorganic materials like fillers and metals remain practically unaltered during pyrolysis process and free of the binding organic matter; therefore, metals could be separated and the remaining solid may be reused as additive, filler or pigment. Lopez *et al.* [7] defined pyrolysis is an especially appropriate recycling technique for waste streams containing different plastics and other materials, for which mechanical recycling is not feasible.

Thermal and catalytic degradation of plastic wastes are two kinds of chemical recycling processes. The main drawbacks of thermal degradation are its wide product distribution and requirement of high temperature, especially from 500 up to even 900°C. Since thermal degradation demands relatively high temperature and its products require further quality upgrading processes, catalytic degradation of polymer wastes offers considerable advantages over thermal degradation [8–14]. Yield and distribution of products can be easily controlled as well as significantly reducing the reaction temperature by use of suitable catalysts in

catalytic degradation [15].

Over the past two decades, a large number of plastics catalytic pyrolysis results have been published in the literature. A wide range of catalytic materials have been studied in various research works (homogeneous catalysts [16, 17], acid mesoporous materials [18,19], non-acid mesopores solids [20, 21], FCC catalysts [22, 23], zeolites [24, 25], metallic oxides [26, 27]), etc.

From industrial implementation point of view, the use of expensive catalysts may restrict the economy of catalytic processes and also choice of continuous or batch operating plant. Ali *et al.* [28] concluded that the catalyst cost (type and amount) is a key factor when the economy of both technologies (catalytic cracking and thermal cracking) is compared. Additionally, Cardona and Corma [29] concluded that a plastic waste catalytic pyrolysis process could only be supported if the catalyst cost was practically zero. For this reason, the search for “cheap catalysts” for plastic wastes catalytic pyrolysis is the key factor of the process.

Sharrath *et al.* [30] investigated the catalytic degradation of high density polyethylene (HDPE) on a fluidized bed using HZSM-5 zeolite catalyst. Higher gases and liquid yields were achieved at higher temperature in the presence of catalyst. Murata *et al.* [31] investigated the cracking of polyethylene (PE), polypropylene (PP) and polystyrene (PS) in a continuous flow stirred tank reactor. It was found that the degradation by continuous flow operation is a suitable technique for converting waste polymers into liquid hydrocarbon. Other important parameters are the residence time, and the

chemical structure of polymers. The effects of these parameters must be investigated in the presence of catalyst [32].

Red Mud (by-product of the alumina production in Bayer process) has been used in hydrogenation reaction as catalyst.  $\text{Fe}_2\text{O}_3$  is the main component of red mud along with other components like  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  or  $\text{TiO}_2$  [33–36] which can be used as a catalyst in plastic waste cracking. A few studies have been conducted using Red Mud as a catalyst in pyrolysis [17, 37, 38]. In this work, we studied the effect of Red Mud in a catalytic pyrolysis of GPPS.

## 2. Experimental

### 2-1. Sample and catalyst

For preparation of polystyrene sample, polystyrene cups were cut into small pieces by scissor for reaction. Some of the properties of the PS polymer samples are given in Table 1.

Synthesized Red Mud was used as a catalyst in all experiments as it was without any activation or alteration. Red Mud catalyst was thoroughly mixed with PS sample in a proportion of 15 wt% in all the experiments (15 g of catalyst/100 g of plastics).

**Table 1**

General properties of used polymer samples.

Properties	PS
Grain size (mm)	4-6
MFI (Mold Flow Index) ( $\text{g (10 min)}^{-1}$ )	11 <sup>a</sup>
Density ( $\text{g cm}^{-3}$ )	1.04
Humidity (%)	<0.1

<sup>a</sup> At (200°C/5kg)

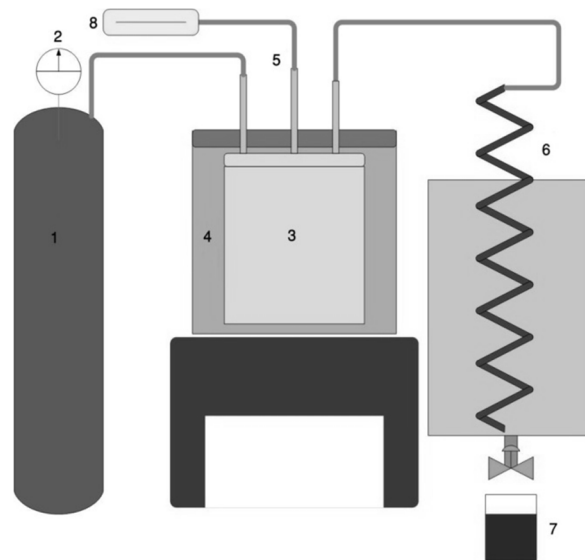
### 2-2. Thermogravimetric analysis and pyrolysis experiments

Thermogravimetric analysis of polystyrene sample was performed using a Mettler

Toledo DSC/TGA1 type instrument. About 10 mg of sample was heated at a rate of  $10^\circ\text{C}/\text{min}$  from 40 to a final temperature of  $600^\circ\text{C}$ . The sample temperature was directly monitored with thermocouple at the vicinity of crucible very close to the sample. The flow of nitrogen gas was maintained at  $5 \text{ dm}^3 \text{ min}^{-1}$  during the analysis. The TGA analytical information gave thermal degradation of PS sample in the absence of catalyst.

### 2-3. Experimental procedure

The catalytic pyrolysis experiments were carried out in a semi-batch unstirred stainless steel reactor (6.28 liter) operated at atmospheric pressure with Red Mud catalyst. The catalyst was mixed with the PS sample in a proportion of 15 wt% in all the experiments (15 g of catalyst/100 g of PS sample). The pyrolysis set up is shown in Fig. 1.



**Figure 1.** Flow sheet of the experimental set-up used. (1) Nitrogen cylinder, (2) rotameter, (3) reactor, (4) electric furnace, (5) reactor thermocouple, (6) condenser, (7) collection vessel for liquid products, and (8) temperature controller.

In a typical run, 200 g of PS sample were thoroughly mixed with 30 g of Red Mud catalyst and charged into the reactor. The reactor was heated with an electrical furnace at a rate of  $5^{\circ}\text{C min}^{-1}$  to the desired temperature. The reactor temperature was controlled and monitored by a set of temperature controller and thermocouple. Nitrogen gas flow was maintained at a rate of  $1 \text{ dm}^3 \text{ min}^{-1}$  in the reactor in order to have oxygen free atmosphere. The effluent gases were cooled in a condenser unit to separate condensable gases from non-condensable gases. The condensable gases were then collected in the form of liquid for chemical analysis. The solids, liquids and gaseous products were collected after each experimental run and then characterized.

#### 2-4. Characterization methods

Condensable gases in the form of liquid were analyzed by Agilent 6890 gas chromatography coupled with mass spectrometry detector (GC-MS). The set up parameters are given in Table 2. Agilent 5973 gas chromatograph (Sigma 3B) coupled with thermal conductivity detector (GC-TCD) was used to analyze non condensable gases. The set up parameters are given in Table 3.

**Table 2**  
GC-MS method characteristics.

Column	HP5MS
Carrier gas	He
Carrier gas flow	1.0 mL/min
Initial temperature/initial time	$50^{\circ}\text{C}/2 \text{ min}$
Heating rate	$10^{\circ}\text{C}/\text{min}$
Final temperature/final time	$300^{\circ}\text{C}/10 \text{ min}$
Injection temperature	$250^{\circ}\text{C}$
Injection volume	$< 1.0 \mu\text{L}$
Detector temperature (quad/source)	$150^{\circ}\text{C}/230^{\circ}\text{C}$

**Table 3**  
GC-TCD method characteristics.

Column	Propak Q
Carrier gas	He
Carrier gas flow	50 mL/min
Initial temperature	$100^{\circ}\text{C}$ (Constant)
Final temperature	$100^{\circ}\text{C}$ (Constant)
Injection temperature	$120^{\circ}\text{C}$
Injection volume	Variable
TCD detector temperature	$150^{\circ}\text{C}$

The Flash point was determined by Cleveland open cup method ASTM-D92-81. Density and API gravity (ASTM-D-257-82), kinematic viscosity (ASTM-D-445), cloud point (ASTM-D2500-81) and pour point (ASTM-D-97) were also determined according to ASTM standard methods for fuel.

### 3. Results and discussion

#### 3-1. Thermogravimetric analysis of polystyrene

Fig. 2 shows polystyrene thermal decomposition weight losses at different temperatures under linear heating rate. This figure shows that the decomposition is gradually started from  $175$  up to  $400^{\circ}\text{C}$ . The curve shows that maximum weight loss related to volatilization of hydrocarbons occurred between  $400$  and  $450^{\circ}\text{C}$  (99.0% weight change). The weight change was steep, from  $400$  to  $450^{\circ}\text{C}$ . This shows the styrene polymer combustion produced excess heat momentarily. The residue weight was 0.02% and was found constant up to  $600^{\circ}\text{C}$ . This indicates that a certain amount of char like carbeneous material is formed during the decomposition of polystyrene.

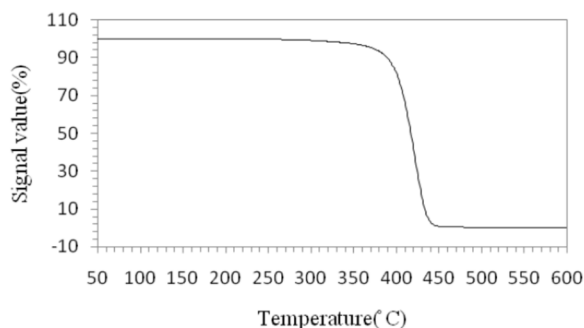


Figure 2. TGA curve of polystyrene.

### 3-2. Synthesis of red mud (catalyst)

Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, SiO<sub>2</sub> and CaO powders were used as precursors for synthesis of Red Mud. The powders were proportionally mixed in ethanol for 4 h and the slurry was then dried at 100°C for 1 h. Subsequently, the obtained powder was ground to get fine powder appropriate for catalyst. X-ray diffraction analysis was used for phase analysis of the synthesized Red Mud, using a Cu K $\alpha$  monochromatized radiation source. Synthesized Red Mud composition is presented in Table 4. As can be seen, it is mainly composed of Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> with other oxides. The XRD pattern of synthesized Red Mud is shown in Fig. 3.

Table 4

Composition of Red Mud (wt%) (dried basis).

Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	SiO <sub>2</sub>	CaO	Others <sup>a</sup>
41.4	26.8	14.6	9.2	6	2

<sup>a</sup> By difference

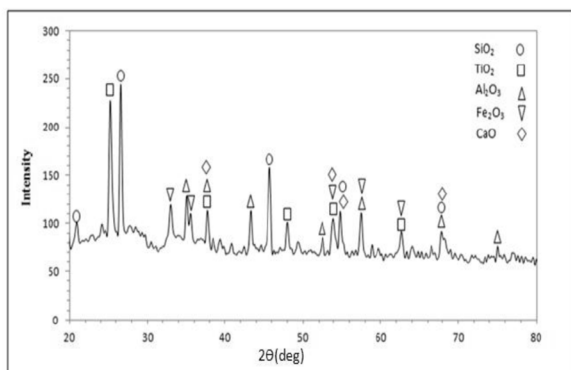


Figure 3. XRD pattern of synthesized Red Mud.

### 3-3. Pyrolysis yields

The liquid (condensable gases), gas and solid yields (wt%) obtained at the different temperatures are shown in Table 5. The solid yield was almost constant in all the experiments. The gas and liquid yields were strongly influenced by reaction temperature. The ratio of gas to liquid yield was increased at higher temperature. As reaction temperature increased, gas yield was also increased while liquid yield was decreased. This has also been reported by many other authors (e.g. [39–41]). It is attributed to stronger C–C bonds cracking at higher temperatures. This yields higher hydrocarbons with shorter carbon chains.

Table 5 shows that a small quantity (0.7–1.0 wt%) of solid products was obtained in all the experimental runs although the original sample did not contain any inorganic matter (char formation). This is attributed to the secondary re-polymerization reactions of polymer products. Char formation in polymeric wastes pyrolysis is a well documented fact that has been reported by many research groups (e.g. [42–47]).

Table 5

Effect of temperature on pyrolysis yields (wt%).

Temperature (°C)	Liquids	Gases	Solids
350	93.0	6.0	1.0
400	86.0	13.2	0.8
450	80.0	19.3	0.7

### 3-4. Pyrolysis liquids

A summary of GC–MS analysis results is presented in Table 6. The values presented in Table 6 are % area and not wt%, thus the relative amounts of the different products are not directly reflected by these values. This is

due to the response differences of organic compounds in GC–MS analysis. Table 6 shows that styrene is the most abundant product with percentage areas ranging from 54% to an area of almost 60%. Subsequent abundant products are benzene and its derivatives (33-36% area) and toluene (1.67-2.30% area). As the reaction temperature increased, the styrene % area was decreased while other components % area increased. Broadly speaking, any change in styrene yield is approximately counterbalanced by benzene and toluene yields (aromatic products). Onwudili *et al.* [11] suggested that benzene and toluene may be formed by the reaction of styrene itself, rather than from the direct degradation of the original sample. This study also proved Onwudili *et al.*'s suggestion. As seen in Table 6, the proportion of styrene with aromatic compounds changes as the reaction temperature increases. It is also worth noting that styrene yield decreases from 350 to 450° C which indicates that styrene was formed at lower temperatures and then was decomposed to other chemicals, mainly benzene and toluene. The results obtained by other authors in catalytic pyrolysis of polystyrene [48, 49] also indicated that the decrease of styrene yield is due to secondary reactions. It is also worth noting that proportion of naphthalene (0.83% area) in the experiment carried out at 450 °C, which contributed to the proportions of poly aromatic hydrocarbons (PAH) present in the liquid obtained at this temperature.

### 3-5. Gas composition

Table 7 shows that pyrolysis gases are composed of hydrocarbons ranging from C1 to C6, hydrogen and some carbon dioxide

and monoxide. It can be seen that percentage area of C1–C3 gases (67.4 wt%) was increased at 450 °C as compared to C4–C6 gases (29.3 wt%). Basically, as reaction temperature was increased the percent area of C4–C6 gases was decreased.

**Table 6**

Main components of the pyrolysis liquids determined by GC–MS (% area).

Temperature (°C)	350	400	450
Toluene	1.67	1.71	2.30
Naphthalene	0.34	0.35	0.83
Styrene	60.32	59.15	54.25
Benzene and its derivatives	33.63	34.99	36.56
Others	4.04	3.8	6.06

This is in accordance with the stronger cracking that is produced at the highest temperature. This tendency to produce lighter hydrocarbons can be clearly observed in methane and ethylene yields, which vary from 8.2 and 11.8 wt% at 300°C to 12.0 and 16.4 wt% at 450°C respectively. This behavior was also observed by Mastral *et al.* [50] in the pyrolysis of polyethylene in a fluidized bed reactor. It is also observed from Table 7 that the gases derived from the experiment carried out at 450°C produced more hydrogen than runs carried out at lower temperature. This is attributed to the hydrogen release from aromatic formation reactions which is favored at high temperatures.

### 3-6. Pyrolysis solids

The pyrolysis solids hardly differ from one another, and carbon is the main constituent of solid. Carbonaceous product (char) is formed during pyrolysis along with a small quantity of other elements. The pyrolysis

solids may seem at first sight a useless product of the pyrolysis process. At best, the inorganic material and the catalyst could be recovered and the organic fraction could be used for energy recovery. Bernardo *et al.* [51, 52] have recently published some works warning about the potential ecotoxicology of pyrolysis derived chars due to their content in heavy metals and organic contaminants. A pretreatment step is suggested to improve the material quality which would probably be necessary prior to their final disposal.

**Table 7**  
GC-TCD analysis (wt%) of pyrolysis gases.

Temperature (°C)	350	400	450
H <sub>2</sub>	0.3	0.4	0.6
CO	1.4	0.9	0.7
CO <sub>2</sub>	1.8	2.4	2.0
Methane	8.2	11.2	12.0
Ethane	9.8	12.0	10.2
Ethene	11.8	12.6	16.4
C3	30.2	28.9	28.8
C4	20.4	22.4	20.2
C5	8.0	5.2	5.8
C6	8.1	4.0	3.3

### 3-7. Characterization of obtained liquid from Polystyrene Catalytic Pyrolysis

The obtained liquid from catalytic pyrolysis was characterized as it was without any further processing. The fuel properties like density, specific gravity, API gravity, viscosity, kinematic viscosity, flash point and freezing point of the obtained liquid were measured, as given in Table 8. Also, the standard parameters of gasoline, diesel and kerosene were shown in Table 9 [15]. The density of obtained liquid was about 0.82 g/cm<sup>3</sup> which can be classified as kerosene (densities 0.78-0.82 g/cm<sup>3</sup>) or Diesel (0.834 g/cm<sup>3</sup>). Specific gravity value of the obtained

liquid was about 0.83, as shown in Table 8. This value falls in the range of diesel specific gravity (0.85). The API gravity value was found to be 39.81 for obtained liquid. This API gravity value is in the range of Kerosene API gravity (39.66-41.7) as shown in Table 8. Viscosity and kinematic viscosity values of obtained liquid were 1.267 centipoises and 1.536 mm<sup>2</sup>/s respectively. Viscosity value is in the range of kerosene (0.9-1.5 centipoise). The obtained liquid kinematic viscosity value is close to kerosene value. The obtained liquid flash point value was 36°C which corresponds to the gasoline flash point value (20.8-38°C). The freezing point value in Table 8 is -50°C which is in close agreement with kerosene freezing point value.

**Table 8**  
Fuel properties of liquid yield from catalytic pyrolysis of polystyrene sample.

S. no.	Parameters	Oil derived with Red Mud catalyst
1	Density (g/cm <sup>3</sup> )	0.825
2	Specific gravity	0.830
3	API gravity	39.81
4	Viscosity (centipoise)	1.267
5	Kinematic viscosity (mm <sup>2</sup> /s)	1.536
6	Flash point (°C)	36
7	Freezing point (°C)	-50

### 4. Conclusions

Catalytic pyrolysis is an attractive alternative for plastic waste recycling. The reaction conversion was about 90 wt% and reaction yield consists of liquid (condensable gases), gases and solid.

The liquid yield can be used as an alternative fuel or as a source of valuable chemicals, such as styrene or toluene. As an alternative fuel, it is necessary to adjust some of the physical parameters of the obtained liquid to

match with kerosene. The density, viscosity, API gravity and freezing point of liquid yield fall in the range of kerosene standard parameters. The specific gravity, kinematic viscosity and flash point of liquid yield was different from standard parameters of kerosene. This shows the obtained liquid can be directly used as a fuel or blend with kerosene or diesel oil.

**Table 9**

Standard parameters of gasoline, diesel and kerosene oil [19].

S. no.	Parameters	Gasoline	Diesel	Kerosene
1	Density (g/ml)	0.736/0.725	0.834	0.780-0.82
2	Specific gravity	0.70	0.85	0.78
3	API gravity	65	23-30	41.7-39.66
4	Viscosity (centipoise)	0.7750-0.8394	2.0-4.5	0.9-1.5
5	Kinematic viscosity (mm <sup>2</sup> /s)	5.0	3.77-5.0	2.2
6	Flash point (°C)	20.8-38	55-60	50-55
7	Freezing point (°C)	-58	-54	-50

The obtained gases can be redirected to the pyrolysis processes or as a feed for further processing plants.

The use of catalysts significantly improved conversion to 90% at temperature range of 350 to 450°C. Red Mud (inexpensive by-product of aluminum refining industry) showed a noticeable activity in catalytic plastic waste pyrolysis.

As pyrolysis temperature was increased, gas yield was significantly increased at the expense of liquid yields. The optimum temperature was found to be 450°C for this

catalytic pyrolysis in terms of both conversion and quality of the pyrolysis liquids. The standard parameters of liquid product were comparable with the standard of kerosene and diesel fuel oil. From the density, API gravity, viscosity and flash point tests it was observed that the liquid obtained can be safely classed as kerosene or blended with kerosene. The specific gravity, density and viscosity values of liquid yield were close to diesel.

It is concluded that catalytic pyrolysis of GPPS leads to valuable resource recovery and reduction of waste problem.

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