

Recycling of waste plastics into chemical feedstock

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Abstract

The disposal of waste plastics poses serious problem to the environment. Among the various recycling techniques, the liquefaction of waste plastics is a suitable option for the recovery of feedstock for refinery. The presence of chlorinated plastics in the municipal waste plastic poses various problems during the liquefaction process as they produce corrosive HCl and chlorinated hydrocarbons. Dehalogenation process is a key technology in feedstock recycling of mixed halogenated waste plastics. Two different approaches have been made to solve the mixed halogenated waste plastics recycling. The first approach (two step process) is the degradation of waste plastics (first step) and dehalogenation process (second step) for the plastic-derived oil in a fixed bed flow type reactor. The second approach (single step process) is the simultaneous degradation, and dehalogenation of waste plastics with chlorinated (PVC) and brominated plastics.

Introduction

Plastics with its exclusive qualities of being light, yet strong and economical have invaded every aspect of our day-to-day life. They have many advantages such as durable, light, and easy to mould and can be adapted to different user requirements. Once hailed as a 'wonder material', plastic is now a serious worldwide environmental and health concern, essentially due to its non-biodegradable

nature. Plastic industry is growing phenomenally, as they are widely used in the modern world in agriculture, automobiles, electronics, building materials, packing and so on. Most of the plastics are not biodegradable; all these activities have led to the generation of an increased amount of plastic waste, particularly in more industrialized countries. If this situation is not dealt with in an effective manner, the enormous accumulation of quantities of plastics could lead to serious ecological problems [1-4].

The two most common ways to process plastic waste, namely landfills and incineration, are associated with various environmental problems. It has become increasingly difficult to find suitable places for building technically adequate landfill sites. Due to the resistance from nearby populations and the danger of leaching and soil impregnation, and the subsequent contamination of underground water. Furthermore, this process does not allow the recovery of organic content of plastic waste, which is even more important due to the small lifetime of known petroleum reserves [1].

Incineration of plastic waste to produce heat may be a possibility, but its organic content would totally be destroyed and converted only into CO₂ and H₂O. In addition, depending on its nature, combustion may produce pollutants like light hydrocarbons, nitrous and sulfur oxides, dusts, dioxins and other toxins, that have a highly negative impact on the environment. As with the

incineration, biodegradation is also not the obvious solution for this type of waste, since the synthetic products obtained in the petrochemical industries are generally resistant to this type of action.

There has been a plethora of research work on the possible methods for the recycling of various plastics. Recovery of fuels and chemicals through catalytic pyrolysis of plastic wastes by Michael *et al* [5], production of engine fuel from waste plastics by thermal treatment [6], pyrolysis of mixed plastics into aromatics [2], chemical recycling of plastics into useful organic compounds by oxidative degradation [7], polymer waste recycling over "used" catalysts [8], pyrolysis of waste derived fuel mixtures containing PVC [9], and effect of plastic waste composition on product yield [10] was performed by various researchers.

Feedstock recycling is based on the decomposition of polymers by means of heat, chemical agents and catalysts to yield a variety of products ranging from starting monomers to mixtures of compounds, mainly hydrocarbons, with possible applications as a source of chemicals or fuels. Recently several petrochemical companies have considered the feedstock recycling of plastic waste in existing refinery facilities, which would obviate the necessity of building new processing plants. This alternative is based on the similarity of elementary composition between plastics and petroleum fractions. However, the presence of PVC in the municipal waste plastics poses various problems during the pyrolysis. The waste from electrical and electronic equipment contains the brominated flame retardant containing high impact polystyrene (HIPS-Br) plastic, which produces various brominated hydrocarbons and also possible formation of dioxins, which then have to be further processed prior to being used as a feedstock or fuel.

In the present study, we discuss the recycling of waste plastics into feedstock and also the dehalogenation process during the recycling. Based on the laboratory scale studies, the pilot plant scale setup for the liquefaction of waste plastics and dehalogenation process was developed. The iron and calcium based carbon composite catalyst/sorbent developed for dehalogenation process and optimized

the degradation, dehalogenation conditions for the complete removal of halogen content to produce halogen free liquid products, which can be used as feedstock in refinery. The applicability of the halogen free plastic derived oil for the generation of power by diesel engines was studied.

Experimental

The PVC containing mixed plastic (MX/PVC) derived oil was prepared by degrading mixed plastics containing PE (33%), PP (33%), PS (33%) and PVC (1%) as a model sample at 410°C with a feed rate of 1 kg/h (Figure 1). Approximately 85 wt% of liquid products, residue 10 wt% and gas 5 wt% was obtained. The oil derived from mixed plastic degradation contained ca.2000 ppm of organic chlorine compounds. The dechlorination of mixed plastic derived oil was carried out using a fixed bed reactor (Figure 2) at atmospheric pressure with a reaction temperature of 300-350°C and a liquid hourly space velocity (LHSV) of 5-40 h⁻¹. In a typical experiment, about 1 cm³ (0.1mm average size) of the catalyst was loaded in between two quartz wool beds and treated in He atmosphere (60 ml/min) at reaction temperature (350°C, 1 h) before feeding the mixed plastic derived oil by a micro-feeder. The liquid product was collected at the downstream of the reactor. A separate cold water condenser was used to ensure the condensation of all volatile liquid products. Iron oxide carbon composites (Fe-C(1)[TR00301], Fe-C(2)[TR97305] and Fe-C(3)[TR99300] contained Fe₃O₄. However the method of preparation is different) and also iron oxide catalysts (α -Fe₂O₃, γ -Fe₂O₃) were used for the dehalogenation of MX/PVC derived oil (PDO). The iron oxide and calcium carbonate carbon composite catalysts were used for the simultaneous degradation and dehalogenation process. The iron oxide and calcium based catalysts/sorbents were cooperatively developed with the Toda Kogyo Corporation, Hiroshima, Japan.

The single step process for the degradation and dehalogenation of halogen content was carried out using the experimental setup shown in Figure 3. Thermal and catalytic degradation of waste plastic was carried out in a glass reactor (length: 35 cm; id 3 cm) under atmospheric pressure by batch operation.

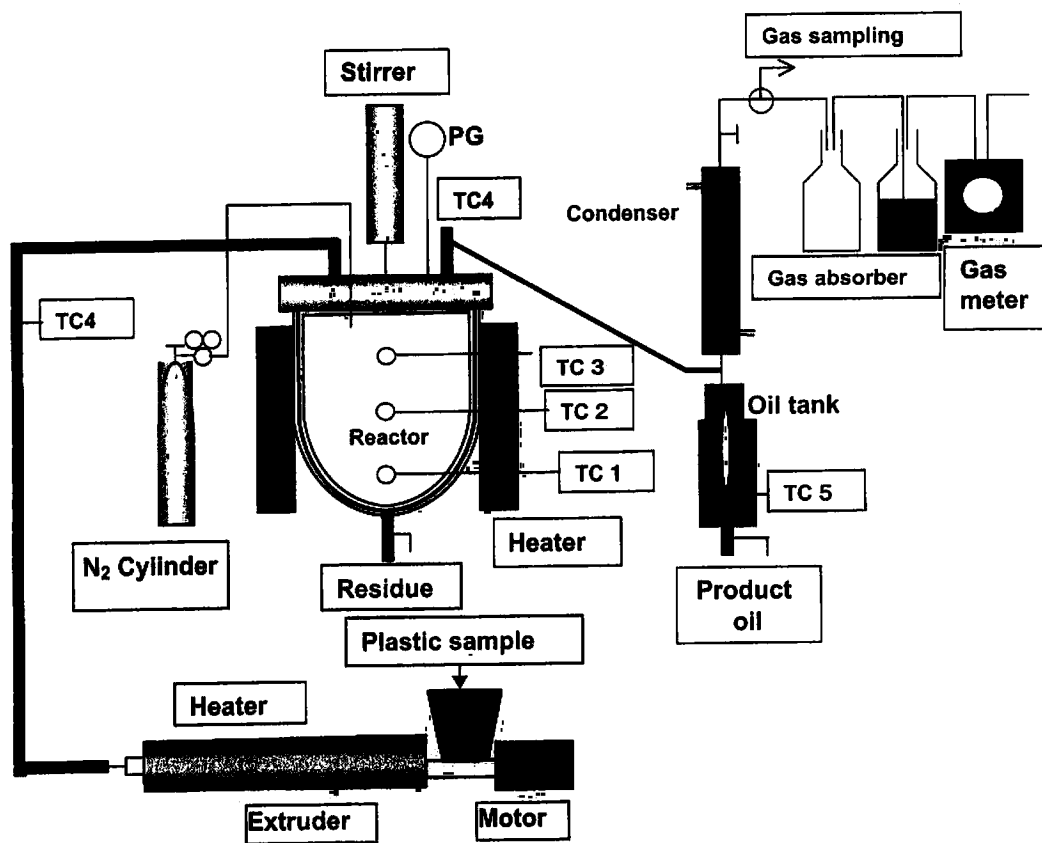


Figure 1. Schematic experimental setup for the conversion of plastics into oil (MX/PVC) at 410°C (step 1 of two step process)

Briefly, about 10 g plastic was loaded into the reactor for catalytic degradation in vapor phase contact. The solid catalyst (1 mm av. dia.) was loaded into the reactor, 10 cm above the plastic bed and the plastic sample was kept at the bottom of the reactor. In a typical run, the reactor was purged with nitrogen gas at a flow rate of 30 mL/min and held at 120°C for 60 min to remove the physically adsorbed water from the catalyst and plastic sample. The reactor temperature was increased to the degradation temperature (430°C) at a heating rate of 3°C/min. In a similar way, the thermal degradation of plastics was carried out in the absence of catalyst. Waste plastic bed temperature was taken as the temperature of the degradation. The gaseous products were

condensed (using cold water) into liquid products and trapped in a measuring jar. The hydrogen bromide and hydrogen chloride evolved from the degradation of the plastic mixture was trapped in a flask containing an aqueous solution of NaOH or ion exchanged water. The analysis of liquid products was carried out using gas chromatograph equipped with FID, AED and MSD. Other details on the experimental procedures and analysis methods can be found elsewhere [4,11,13-15]. Based on the above process results, the pilot plant (250 kg/12 h) was developed for the conversion of waste plastics into feedstock and dehalogenation at the Mizushima, Japan. In the following discussion the abbreviation 3P is used for mixture of PE, PP and PS.

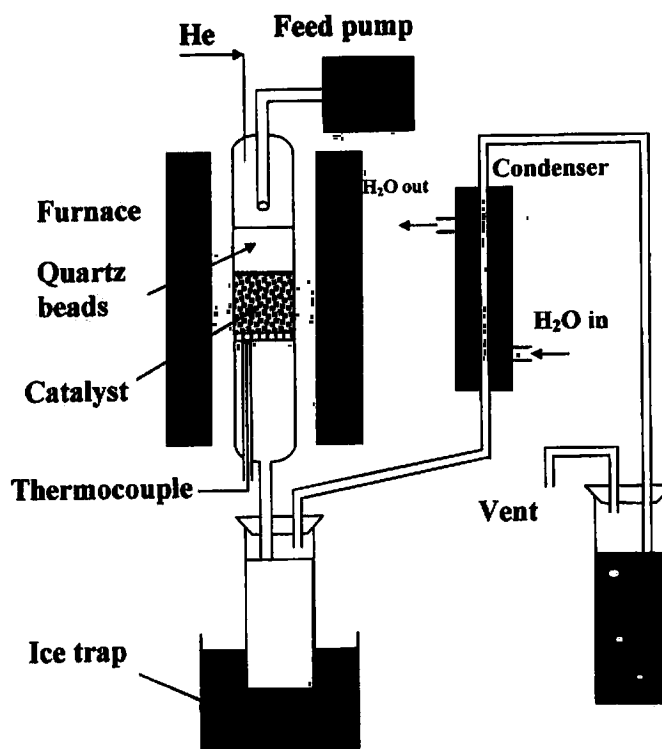


Figure 2. Fixed bed experimental setup for the dehalogenation of plastic derived oil at 350°C (step 2 of two step process)

Results and Discussion

The systematic investigation on the feedstock recycling of waste plastics into valuable chemical feedstock and dehalogenation process was performed. The waste plastic degradation experiments were carried out using a single step (simultaneous degradation and dehalogenation) and two step process i.e., degradation in first step and dehalogenation in second step. Both model mixed plastics and municipal waste plastics obtained from Sapporo city of Japan were used in these experiments. The basic concept of the research is presented in Scheme 1. The development of degradation and dehalogenation process was started with the two step process such as thermal degradation (first step), dehalogenation (second step) by various iron oxides and iron oxide carbon

composites and the results are discussed in the following section.

Degradation of MX/PVC and dechlorination of PDO by iron oxides (A two step process)

Firstly, the PVC containing mixed plastic derived oil (PDO) was prepared by thermal degradation of the mixed plastics as described in the experimental section. The degradation of plastics can be done by catalytic and non catalytic with various microporous and mesoporous materials [16-19], which effect the product gas, liquid and residues, recovery rate of liquid products, and boiling point ranges of liquid products. The degradation of PVC containing mixed plastics (PE, PP and PS) may also leads to the formation of

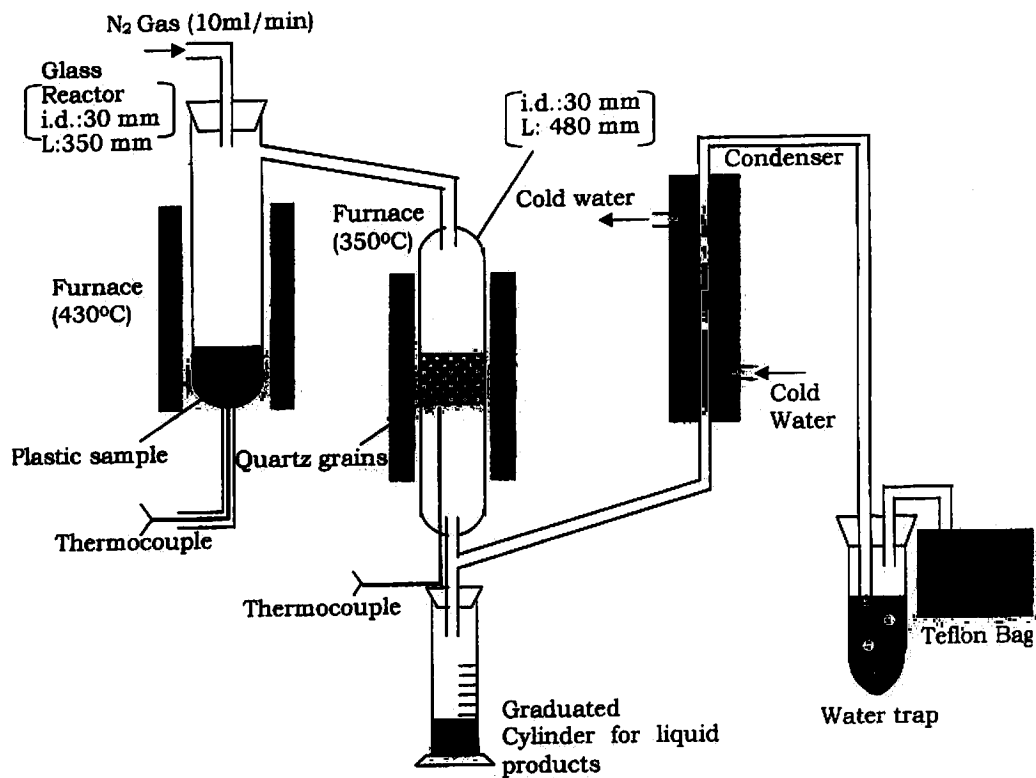
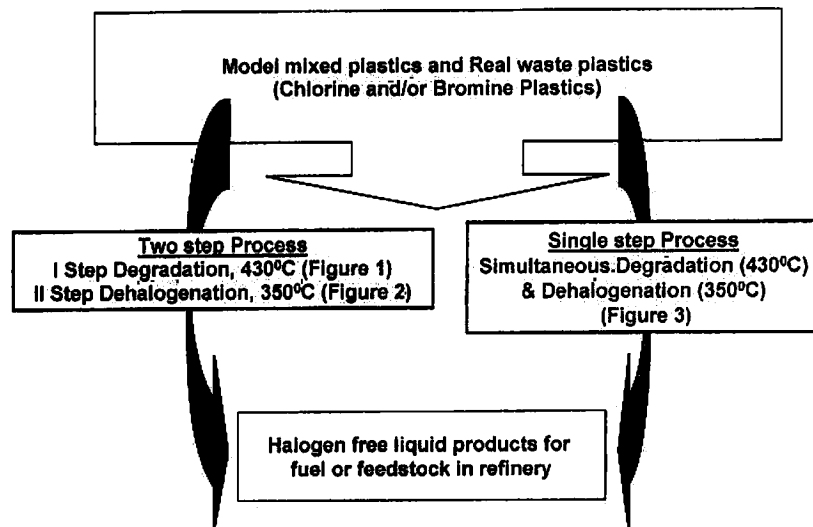


Figure 3: Simultaneous degradation and dehalogenation of mixed halogenated waste plastics into fuel oil



Scheme 1

chloro-organic compounds, in addition to HCl during degradation. It is well known that during the thermal degradation of PVC, elimination of HCl occurs and leads to the formation of conjugated double bonds. The other plastics such as polystyrene (PS) also produce double bond compounds such as styrene during degradation. The polar HCl molecule when liberated from PVC, it attacks the double bonded compounds leading to the production of chloroorganic compounds. The physico chemical properties of PDO are given in Table 1. Catalytic dechlorination is a promising method for the removal of organic chlorine compounds compared to other methods. In the

present study, we used various iron oxide catalysts for dehydrochlorination of chloroorganic compounds in PDO in a second step.

The physical properties of iron oxide catalysts such as α -Fe₂O₃, γ -Fe₂O₃, Fe-C(2), and Fe-C(3) (iron oxide carbon composite with similar compositions but prepared by different methods) are given in Table 2. The chlorine compounds were distributed mainly in the bp range of n-C₆ to n-C₁₉. However, the major chloro-organic compounds are in the range of n-C₆ to n-C₁₁. The GC-MS analysis of PDO showed the presence of 2-chloro-2-methyl propane, 2-chloro-2-methyl pentane, chloroethyl

Table 1. The physico-chemical properties of the MX/PVC derived oil

| Property | Value |
|----------------------------------|--------|
| Density (g/cm ³) | 0.8520 |
| Kinematic Viscosity (cst @50 °C) | 1500 |
| Flash Point (°C) | 7 |
| Pour Point (°C) | 10 |
| Moisture Content (wt. %) | 0.24 |
| Conradson Carbon Residue (wt. %) | 0.11 |
| Calorific Value (cal/g) | 10600 |
| Ash Content (wt. %) | <0.01 |
| Chlorine Content (wt. %) | 0.2 |
| Nitrogen Content (wt. %) | <0.03 |
| Sulfur (mg/kg) | <1 |
| Carbonic Acid (ppm) | 42 |
| Terephthalic Acid (ppm) | <5 |

Table 2. Physical properties of the iron oxide and iron oxide-carbon composite catalysts

| Catalyst | Surface Area (m ² .g ⁻¹) | Iron oxide content (wt.%) | Carbon Content (wt.%) | XRD |
|--|--|------------------------------|--------------------------|--|
| γ -Fe ₂ O ₃ | 13 | 100 | 0 | γ -Fe ₂ O ₃ |
| α -Fe ₂ O ₃ | 4 | 100 | 0 | α -Fe ₂ O ₃ |
| TR97305 | 74 | 93.3 | 6.7 | Fe ₃ O ₄ |
| TR99300 | 60 | 93.2 | 6.8 | Fe ₃ O ₄ |

benzene and 2-chloro-2-phenyl propane [11]. Various iron oxides and iron oxide carbon composites (Table 2) were effectively (above 95 %) dehydrochlorinated into their corresponding alkenes and hydrogen chloride. The dechlorination of PDO was carried out at 350^o C using He carrier gas with a LHSV of 40 h⁻¹. As the true value of GHSV is difficult to determine due to the presence of a large number of hydrocarbons, only the LHSV without considering He carrier flow rate was used. The XRD patterns of the fresh and used catalyst revealed the formation of iron chloride in the used iron oxide catalysts. Blazso et al [12] in their study of the decomposition of PVC reported that metal oxides with a large metal ion radius, such as iron oxide, are able to dehydrochlorinate the PVC by attracting chlorine and weakening the C-Cl bond in the chloro-organic compounds, which are mainly aliphatic compounds like PVC. The dechlorination results also showed that the continuous removal of reversible adsorbed HCl from the catalyst surface is necessary to main a stable dechlorination activity of catalyst [13]. The highly selective and stable FeCl₂/SiO₂ catalyst was also employed for the dehydrochlorination of various chloro organic compounds from the PVC mixed waste plastic derived oil [20]. Pd-Fe carbon composite catalysts were also employed for dehydrochlorination of chloro hydrocarbons and these catalysts obtained by modified carbothermal reduction method using ion exchange resins [21]. From these studies we can conclude that the iron oxides worked as catalyst for dehydrochlorination and also as a sorbent for capturing hydrogen chloride. It is clear from the

above studies, it is clear that the majority of chlorine in the form of HCl (inorganic). The process needs a good sorbent and the cost of the sorbent is also an important aspect on the economical aspect for commercialization. By considering these things, we have used the calcium based carbon composite in the simultaneous degradation and dehalogenation process and the results are as follows.

Degradation and dechlorination by Ca-C (A single step process)

The pyrolysis of PVC mixed with PE/PP/PS plastics in a weight ratio of (1:3:3:3) was carried out under atmospheric pressure in a batch process using calcium carbonate carbon composite (Ca-C) sorbent and also thermal degradation (no sorbent). The products of mixed plastic degradation were classified into three groups: gas, liquid, and degradation residue. Table 3 shows the yield of products (gas, liquid, and residues) and average carbon number (C_{np}), density of liquid products obtained during thermal degradation and also using Ca-C sorbent. The thermal degradation yielded liquid products 63 wt% with 0.79 g/cc density. The liquid product obtained during the degradation with Ca-C sorbent was about 67 (run 1) and 75 wt% (run 5). There is no appreciable change in the C_{np}, and density of liquid products obtained during both in thermal degradation and degradation using Ca-C sorbent (Table 3).

The total chlorine content in liquid products obtained during thermal degradation, degradation

Table 3. Products yield and properties of liquid product from PVC mixed PP/PE/PS [10 g] plastic degradation using Ca-C [consecutive 6 runs] and thermal degradation

Weight ratio: PVC:PP:PE:PS = 1:3:3:3 Weight of Ca-C: 4 g
 Degradation Temp: 430°C Dechlorination Temp: 350°C

| Degradation and run number using Ca-C | Yield of degradation products [wt%] | | | Liquid products | |
|---------------------------------------|-------------------------------------|---------------------|------------|------------------|----------------|
| | Liquid[L] | Gas[G] ^a | Residue[R] | Cnp ^b | Density (g/cc) |
| Thermal | 63 | 24 | 13 | 10.4 | 0.79 |
| 1 | 67 | 23 | 10 | 10.8 | 0.80 |
| 2 | 65 | 22 | 13 | 10.7 | 0.79 |
| 3 | 67 | 21 | 12 | 10.7 | 0.79 |
| 4 | 69 | 21 | 10 | 10.9 | 0.80 |
| 5 | 75 | 15 | 10 | 10.8 | 0.81 |
| 6 | 70 | 20 | 10 | 10.6 | 0.80 |

^a G = 100 - (L+R)

^b Cnp = Average carbon number of liquid products based on C-NP gram

using Ca-C sorbent and also consumed theoretical capacity of Ca-C sorbent during each run of mixed plastic degradation was presented in Table 4. As can be seen from Table 4, liquid products obtained during thermal degradation contain 360 ppm of chlorine. However, the chlorine content is zero (not detected) from run 1 to run 4 by using Ca-C sorbent (4 g), indicating that the chlorine compounds (inorganic and organic) were completely removed from the liquid products.

In the present process, inorganic chlorine compounds (HCl) were captured by Ca-C sorbent and the chlorinated hydrocarbons produced during the PVC mixed plastic pyrolysis process were also

dehydrohalogenated by Ca-C. About 71% of theoretical HCl sorption capacity of Ca-C were utilized for the 4 batches of mixed plastic pyrolysis. The chlorine content 150 ppm was observed during run 5 of degradation and the chlorine content increased from 150 ppm to 3000 ppm (run 6), which is higher than the thermal degradation. It clearly indicates that the sorbent cannot be used in the process after 71% of theoretical capacity (Table 4). The presence of a higher content of chlorinated hydrocarbons during run 6 (3000 ppm) than thermal degradation (360 ppm) might be due to the hydrocarbons produced during the pyrolysis process reacting with the calcium chloride (CaCO₃ converted to CaCl₂ during process) and forming the

Table 4. Chlorine content in PVC mixed-PP/PE/PS [10 g] plastic degradation liquid products using Ca-C [consecutive 6 runs] and consumed theoretical sorbent capacity for each run

Weight ratio: PVC:PP:PE:PS = 1:3:3:3 Weight of Ca-C: 4 g
 Degradation Temp: 430°C Dechlorination Temp: 350°C

| Degradation and run-number using Ca-C | Chlorine content in liquid products (ppm) | Consumed theoretical capacity of CaCO ₃ [%] |
|---------------------------------------|---|--|
| Thermal | 360 | --- |
| 1 | 0 | 18 |
| 2 | 0 | 35 |
| 3 | 0 | 53 |
| 4 | 0 | 71 |
| 5 | 150 | 89 |
| 6 | 3000 | 106 |

chlorinated hydrocarbons in the liquid products.

The liquid products were characterized by a Normal Paraffin gram (NP-gram) proposed by Murata et al [14]. Figure 4 illustrates the C-NP gram of the liquid products obtained by analyzing their gas chromatogram. As with the C-NP gram, the carbon number distribution of chlorinated hydrocarbons (Cl-NP gram) in the liquid product was prepared from the GC-AED data and was presented in Figure 5. The NP-gram is a carbon number distribution of hydrocarbons derived from the gas-chromatogram on the basis of boiling points of a series of normal paraffins. We can find out the peak positions of a series of normal paraffins on a gas-chromatogram of the liquid product obtained by thermal degradation of polymers by using a PE derived oil which contains a series of normal

paraffins as a index material. NP gram is constructed by plotting the weight fraction of hydrocarbons, which are located within the range of retention values of two successive normal paraffins, C_{n-1} and C_n, against the carbon number, n. Since the carbon number, n, corresponds to the boiling point range of a certain group of hydrocarbons, the NP gram actually represents a volatility distribution of the liquid product. The hydrocarbons containing the chlorine were distributed in the range of C₆-C₁₁. The presence of chlorinated compounds during the thermal degradation and degradation with sorbent (run 5 to run 6) was observed. 2-chloro-2-phenyl propane was the major chlorine compound observed during thermal degradation and also during run 6. 2-chloro-2-methyl propane, 2-chloro-2-methyl pentane, and α-chloro ethyl benzene was also identified during 5 and 6 runs.

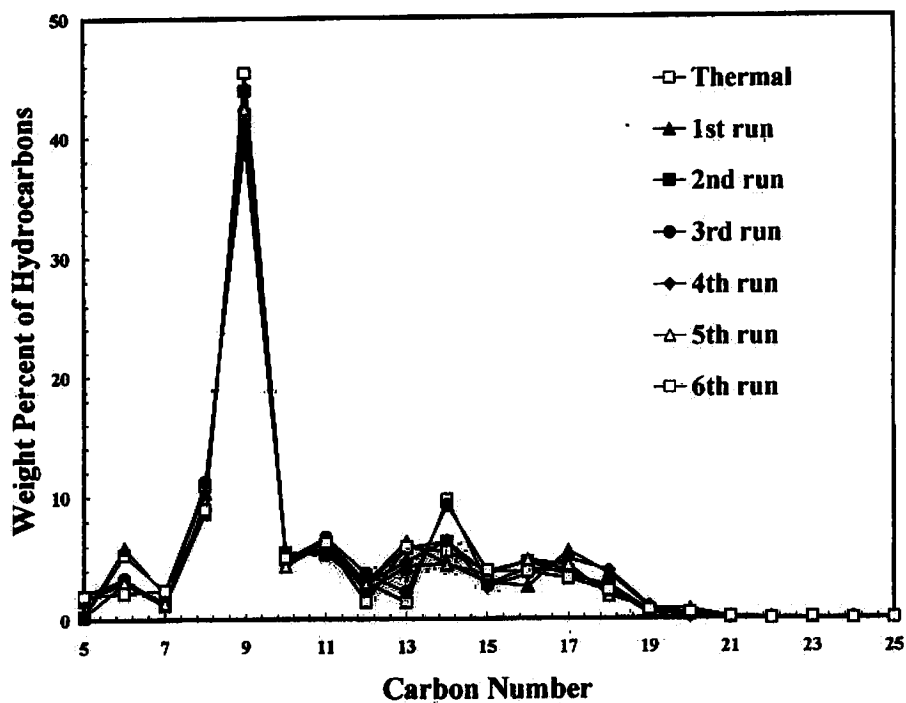


Figure 4. C-NP gram of liquid products obtained during PP/PE/PS/PVC at 430°C

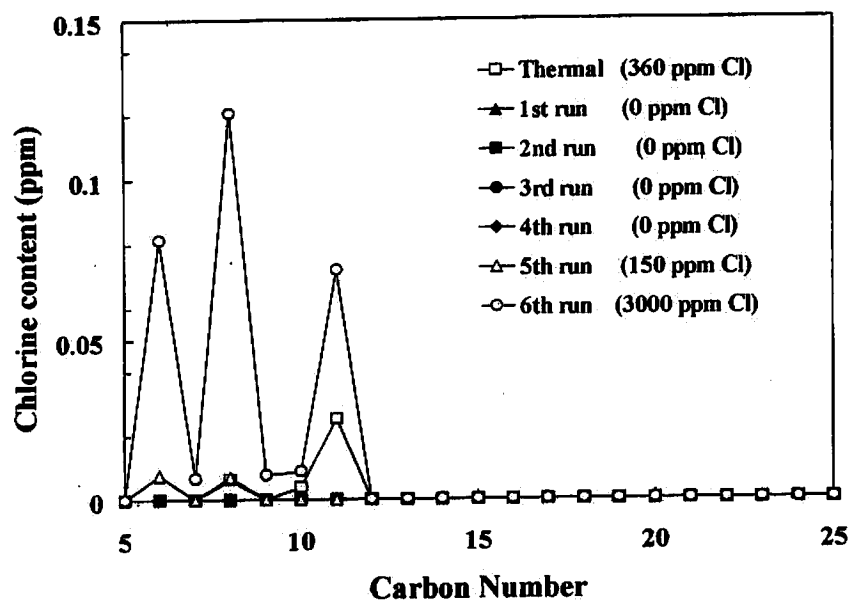


Figure 5. Cl-NP gram of liquid products obtained during PP/PE/PS/PVC at 430°C

Table 5. Thermal and catalytic degradation of 3P/PVC^a and MWP products yield, liquid properties and Cl concentration

| Degradation (430°C) | Dechlorination (350°C) | Product yield, wt% | | | Density (g/ml) | C _{np} | Cl content (ppm) | |
|---------------------|------------------------|--------------------|----------------------|-------------|----------------|-----------------|------------------|-----------------|
| | | Liquid (L) | Gas (G) ^b | Residue (R) | | | Oil trap | Water |
| 3P/PVC | Thermal | 63 | 24 | 13 | 0.79 | 10.4 | 380 | 6100 |
| | Ca-C 4g | 64 | 19 | 15 | 0.80 | 10.1 | ND ^c | ND ^c |
| MWP | Thermal | 63 | 20 | 17 | 0.80 | 11.2 | 1170 | 40 |
| | Ca-C 4g | 60 | 25 | 15 | 0.80 | 10.2 | 590 | 2 |
| | Ca-C 8g | 61 | 25 | 14 | 0.80 | 9.8 | 290 | 1 |

^a Cl content in PVC was 52.4 wt%; ^b G = 100 - (L + R);

^c Not detected (less than the detection limit of instrument)

The X-ray diffraction pattern of Ca-C before degradation indicates the presence of CaCO₃ phase but after use in degradation the CaCl₂.nH₂O (where n = 2, 4) peaks were observed indicating the sorption of chlorine by CaCO₃. The Ca-C sorbent was used successfully for the consecutive 6 batch processes and halogen free liquid products were obtained upto 4 runs by utilizing 71% of sorbent theoretical HCl sorption capacity. The process was successfully carried out for consecutive six runs and produced the halogen free liquid products which can be used as feedstock and also estimated the sorbent capacity. In an another study, the effect of solid acid catalyst for the degradation of PVC mixed plastics and dehalogenation by iron oxides has been performed [22, 23]. Boiling point distributions and dechlorination of organic chlorine compounds in PVC mixed waste plastic derived oil has been reported.

The waste plastics from electric and electronic equipment (WEEE) contains brominated flame retardant plastics such as heating impact polystyrene (HIPS-Br) and it also produces brominated hydrocarbons in addition to hydrobromic

acid (HBr) during the degradation. The growth of WEEE is also increasing in a substantial way. The feedstock recycling of mixed Cl and Br plastics were performed using Ca-C.

Simultaneous degradation and dehalogenation (Cl, Br) by Ca-C (A single step process)

The thermal degradation of mixed plastics (weight ratio PP/PE/PS/PVC/HIPS-Br = 3:3:2:1:1) was performed under atmospheric pressure in a batch process at 430°C and degradation also performed by using Ca-C. The thermal degradation yielded liquid products (71wt%) with the average carbon number 13.7 and density 0.82 g/cc (Table 5). The use of Ca-C sorbent in the degradation process decreased the liquid products from 71wt% to 62wt% (Ca-C 2 g) and 66wt% (Ca-C 4 g). The amount of residue observed with thermal degradation and Ca-C 2g was 12wt%. However, the residue in the degradation process with the Ca-C 4g was about 9wt%. The density of liquid products did not change in the presence or absence of Ca-C sorbent.

The quantitative analysis of chlorine and

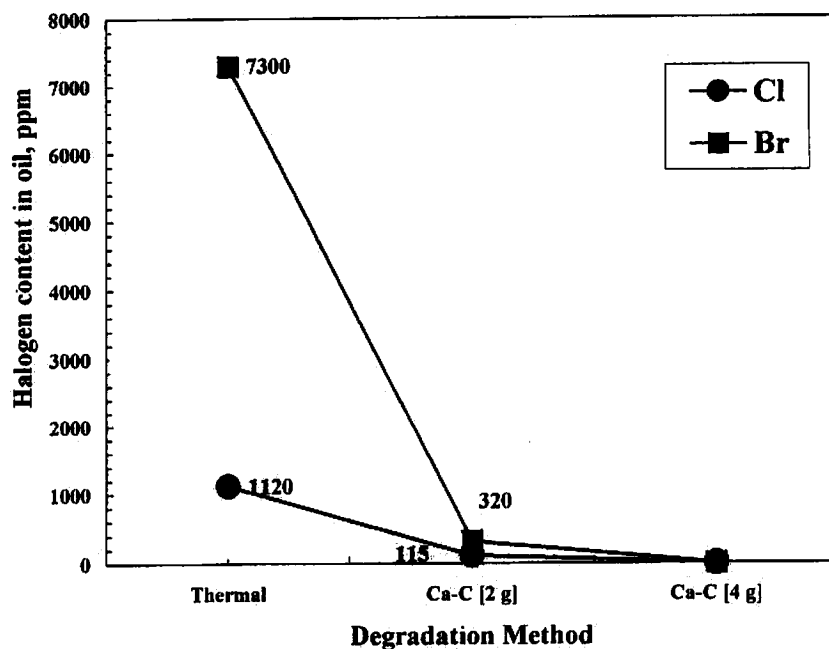


Figure 6. The effect of Ca-C sorbent for dehalogenation (Cl and Br) during PP/PE/PS/PVC/HIPS-Br degradation at 430°C

bromine in the liquid products done by GC-AED. As can be seen from Figure 6, the thermal degradation of mixed plastics yielded the liquid products with 7300 ppm of bromine and 1120 ppm of chlorine. However, with the use of 2g Ca-C in the degradation process, the halogen contents drastically decreased: bromine to 320 ppm; and chlorine to 115 ppm. With the increase of sorbent from 2 g to 4 g in the degradation process, the halogen content completely removed from the liquid products. The chlorinated hydrocarbons found during the thermal degradation were 2-chloro-2-phenyl propane, 2-chloro-2-methyl propane, 2-chloro-2-methyl pentane, and α -chloro ethyl benzene and brominated hydrocarbons were bromocyclohexane, and 1-(bromoethyl) Benzene etc. The X-ray diffraction studies revealed the presence of CaCO₃ phase in fresh Ca-C sorbent. The X-ray diffraction patterns for the used Ca-C shows that the calcium carbonate converted into the calcium chloride and calcium bromide.

From the above studies we found that the Fe-C(1) and Ca-C were effectively used for the

dehalogenation process during the degradation of various halogenated mixed plastics. The inorganic (HCl) chlorine was a major product and the organic chlorine compounds were minor products with Cl and Br mixed plastics. However, it is clear that the sorptive capacity of Ca-C was higher than Fe-C(1) and the catalytic dehalogenation activity was higher with Fe-C(1) than Ca-C. We optimized the reaction conditions to minimize the production of organic halogen compounds so that the Fe-C(1) or Ca-C can effectively work as a catalyst/sorbent. In addition, it is also important to consider the economic factors when developing materials in the pilot plant scale studies. After considering the above all results we performed the degradation of model mixed and real MWP plastics at a pilot plant scale.

Laboratory scale studies on model and real MWP (A single step process)

The laboratory scale pyrolysis studies were performed using model mixed and real MWP

using Ca-C. The results of the thermal and catalytic studies are shown in Table 5. There is no significant change in yield of liquid products in both cases. Thermal degradation of 3P/PVC (10 g) liquid products showed the presence of 380 ppm (organic) and 6100 ppm (inorganic) chlorine, on the other hand 1170 ppm (organic) and 40 ppm (inorganic) was found with MWP (10 g). The use of Ca-C (4 g) in 3P/PVC degradation has completely removed the organic (liquid) and inorganic chlorine (water trap). However, the degradation of MWP with Ca-C did not completely remove the chlorine content, and it contained about 590 ppm of chlorine in liquid products (organic). It is clear from the investigation that the degradation behavior of model mixed plastics (3P/PVC) is different from that of MWP. Further investigation of the MWP composition confirmed the presence of PET in the laminated sheets, and a small amount of ABS in addition to the major 3P/PVC. Both 3P/PVC mixture and MWP derived oil were in the range of C₅ to C₂₀, and C₉ was highest, which is mostly due to styrene monomer as shown in Figure 7. The liquid products in both the cases are compared with the conventional petroleum fractions such as gasoline, kerosene, and diesel oil. The separation into individual fractions is technically feasible but not economical and production of gasoline in the plant is not safe

process. However, it is better to send the halogen free crude plastic derived oil to the refinery as it is economical and better way of utilization of valuable chemicals.

Pilot plant scale studies for model mixed and real MWP

Based on the laboratory scale studies, the degradation of both model waste plastics [(3P [150]/PVC [3]- total 153kg)] and MWP (50kg) was carried out in a large-scale pilot plant (Figure 8) and the results are presented Table 6. In an earlier publication, Sakata et al., reported on the spontaneous degradation of municipal waste plastics at low temperature (320°C) during the dechlorination treatment [4]. Thermal and catalytic degradation of municipal waste plastics into fuel oil by batch and continuous feed operation at 410°C was discussed [24]. The thermal degradation of 3P/PVC (153 kg) mixture was performed and the analysis of degradation products shows that the liquid products contained 530 ppm of chlorine (organic) and the water trap with 2940 ppm of HCl. However, the use of Ca-C (20 kg) removed all organic chlorine and decreased the HCl concentration to 6 ppm, but the water contained about 5-7 ppm HCl. The degradation of MWP (50

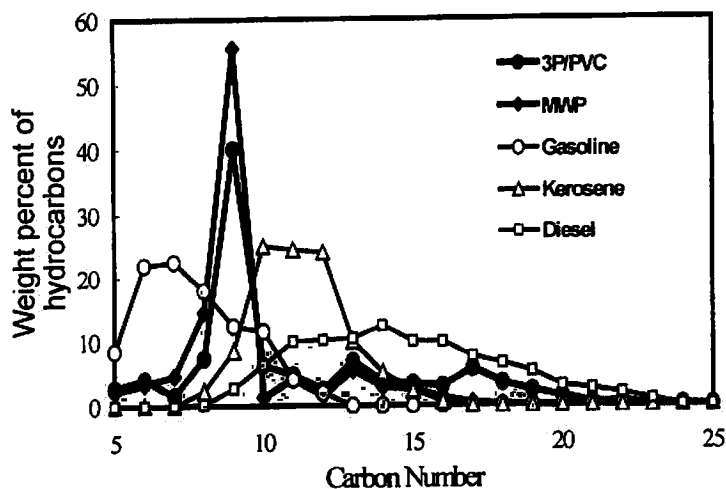


Figure 7. Comparison of C-NP gram of liquid products obtained with MWP, 3P/PVC with gasoline, diesel and kerosene

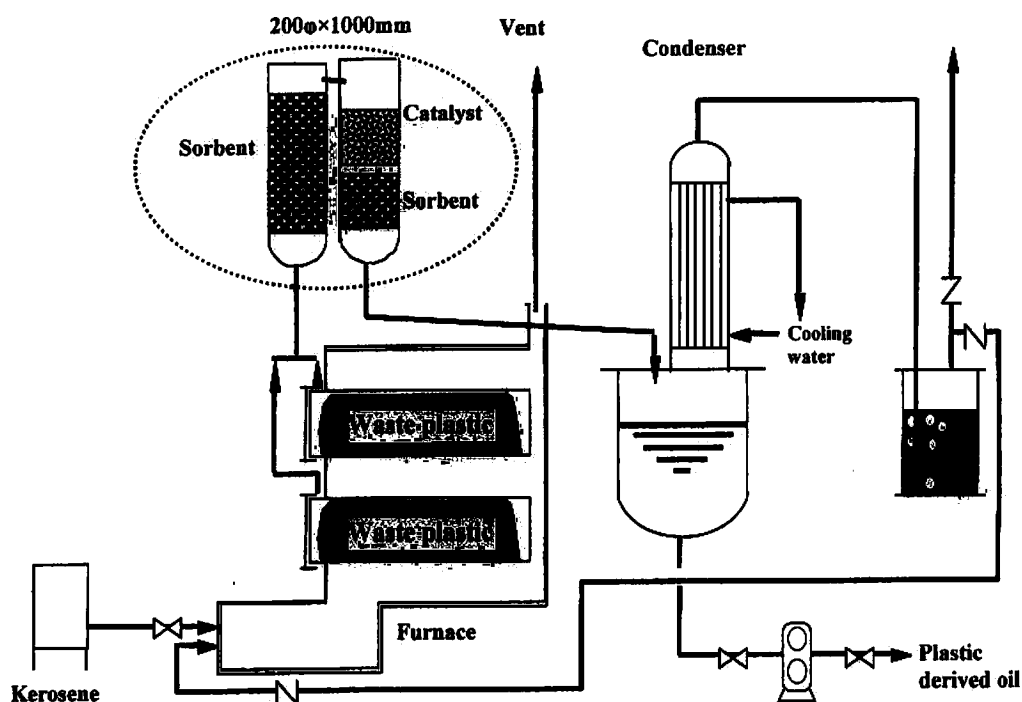


Figure 8. Outline of pilot plant experimental setup for the simultaneous degradation and dehalogenation process (Batch reactor, 250 kg/12h)

Table 6: Raw plastic material used in pilot plant and the product yields along with the Cl concentration for thermal and catalytic degradation of 3P/PVC^a and real Municipal Waste Plastic

| Raw plastic material (Kg) | | | | | | Sorbent Ca-C 8mm (Kg) | Product yield, wt% | | | Cl content, ppm | |
|---------------------------|----|----|-----|-----|-------|--------------------------------|-----------------------|----------------|---|-----------------|------|
| PP | PS | PE | PVC | MWP | Total | | L | G ^b | R | Oil | trap |
| 50 | 50 | 50 | 3 | - | 153 | - | 69 | 28 | 3 | 530 | 2940 |
| 50 | 50 | 50 | 3 | - | 153 | 20 | 82 | 16 | 2 | ND ^c | 6 |
| - | - | - | - | 50 | 50 | 20 | 53 | 39 | 6 | 100 | 7 |

^a Cl content in PVC was 52.4 wt%; ^b G = 100 - (L + R);

^c ND = Not detected (less than the detection limit of instrument)

kg) with Ca-C (20 kg) yielded oil with 100 ppm of organic and water trap contained 7 ppm. As can be seen from the Table 6, that the mixed model plastics yielded about 82 wt% of liquid products with 16 wt% gas and 2 wt% residue. In the case of MWP, the yield of liquid products decreased to 53 wt%, as the MWP contains various other materials such as paper with high moisture content, metals etc. In an alternative application to the feedstock recycling, we have tested for the production of power by diesel engines. The results shows that it had good performance for the generation of power by producing low CO, NO, and oxygen emissions than the diesel fuel. The another degradation product residue was heat-treated and analyzed its contents for further applications such as solid fuel. Approximately, 95 wt% of carbon and the remaining 5 wt% was metals such as Al as major, Fe, Ca, Mg,

Si, Ti etc were observed by energy dispersive analysis of X-rays (EDAX). The calorific value of carbon showed that about 7750 cal/g. The gaseous products can be used for various applications. In Japan, municipal waste plastic separation will be done by individuals and dumped at the designated places. In addition to the scientific and technological development, the waste management is also an important for the recycling of waste plastics to protect the environment and get back the chemical feedstock. Batch operated liquefaction process are suitable for low populated places and large-scale liquefaction plants are good for highly populated or metropolitan areas. Due to the low density (fluffy) of plastic material, the transportation costs will be high. The transportation of crude plastic derived oil is a suitable option for decreasing the transportation costs. The aim of this research is

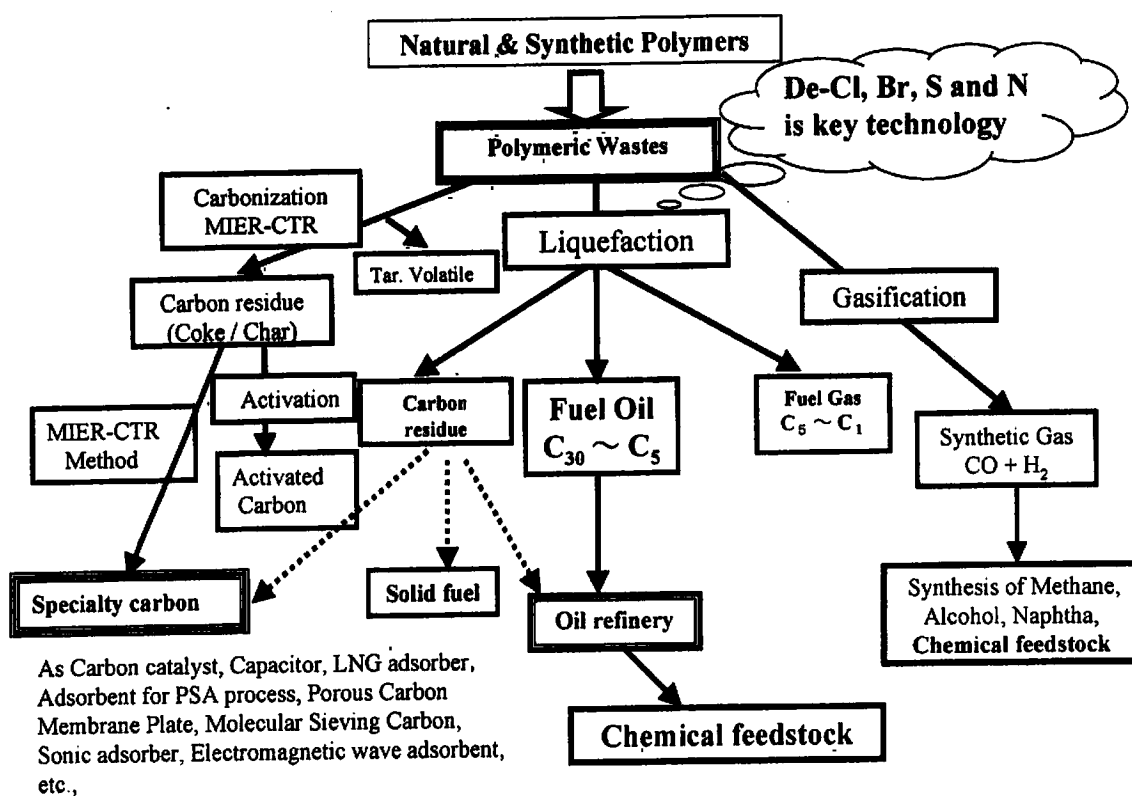


Figure 9. Outline of fundamental and applied research on recycling of waste polymeric materials at our lab

to develop small scale batch type waste plastic degradation plant with a treatment capacity of about 500 kg per batch (12 h) for distribution in local regions as a substitute for the large scale degradation plants with a treatment capacity of few thousands ton per year concentrated in urban areas. The fundamental and applied research on the natural and synthetic polymeric waste materials to various valuable materials, which are in progress in our laboratory, was presented in Figure 9. The studies on the major waste plastics from electric and electronic equipment (WEEE) such as HIPS-Br [25] and ABS-Br [26] and the debromination process to produce bromine free liquid products was successfully performed. The feedstock recycling process for the non-halogenated and halogenated (Cl, Br) mixed plastics and dehalogenation catalyst/sorbent were successfully completed and ready for the commercialization.

Conclusion

The development of catalysts for the degradation of model mixed waste plastics and real MWP and dehalogenation by catalyst/sorbent was successfully performed. The reaction conditions for the degradation and dehalogenation process such as effect of temperature, amount of catalyst/sorbent, compositions of catalyst/sorbent etc were optimized. The degradation behavior and formation of halogenated compounds (organic and inorganic) from model mixed plastics (3P/PVC) and real MWP was found. Calcium carbonate, Iron oxide and iron oxide carbon composites based catalyst/sorbent effectively removed the halogen content during halogenated mixed waste plastic pyrolysis process and also in the pilot plant scale studies. The halogen free liquid products can be used crude oil in a feedstock in refinery from which the basic polymers produced.

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References

1. Uddin, M.A., Bhaskar, T., Kaneko, J., Muto, A., Sakata, Y., Matsui, T. 2002, *Fuel* **81**, 1819.
2. Kaminsky W., Kim J.S., 1999, *J. Anal. Appl. Pyro.* **51**, 127.
3. Kaminsky W., Hartmann F., 2000, *Angew. Chem. Int. Ed.* **39**, 331.
4. Sakata Y., Uddin, M.A., Muto, A., Narazaki, M., Koizumi, K., Murata K., Kaji, M., 1998, *Ind. Engg. Chem. Res.* **37**, 2889.
5. Michael, J.M., Arzoumanidis, G.G., Brockmeier, F.E. 1998, *Environmental Progress.* **17**, 19.
6. Walendziewski, J. 2002, *Fuel* **81**, 473.
7. Pifer, A., Sen, A. 1998, *Angew. Chem. Int. Ed.* **37**, 3306.
8. Ali, S., Garforth, A.A., Harris, D.H., Rawlence, D.J., Uemichi, Y. 2002, *Cat. Today* **75**, 247.
9. Zevenhoven, R., Axelsen, E.P., Hupa, M. 2002, *Fuel* **81**, 507.
10. Pinto, F., Costa, P., Gulyurtlu, I., Cabrita, I. 1999, *J. Anal. Appl. Pyro.* **51**, 39.
11. Lingaiah, N., Uddin, M.A., Muto, A., Sakata, Y., Imai, T., Murata, K., 2001, *App. Catal A: Gen.* **207**, 79.
12. Blazso, M., Jakab, E., 1999, *J. Anal. Appl. Pyro.* **49**, 125.
13. Lingaiah, N., Uddin, M.A., Muto, A., Imai, T., Sakata, Y., 2001, *Fuel* **80**, 1901.
14. Murata, K., Hirano, Y., Sakata, Y., Uddin, M.A., 2002, *J. Anal. Appl. Pyro.* **65**, 71.
15. Uddin, M.A., Sakata, Y., Shiraga, Y., Muto, A., Murata, K. 1999, *Ind. Eng. Chem. Res.* **38**, 1406.
16. Sakata, Y., 1998, *Macromol. Symp.* **135**, 7-18.
17. Uddin, M.A., Koizumi, K., Murata, K., Sakata, Y. 1997, *Polym. Deg. Stab.* **56**, 37-44.

18. Uddin, M.A., Sakata, Y., Muto, A., Shiraga, Y., Koizumi, K., Kanada, Y., Murata, K. 1998, *Micr. Meso. Mat.* **21**, 557.
19. Sakata, Y., Uddin, M.A., Muto, A., Kanada, Y., Koizumi, K., Murata, K. 1997, *J. Anal. Appl. Pyro.* **43**, 15.
20. Lingaiah, N., Uddin, M.A., Morikawa, K., Muto, A., Murata, K., Sakata, Y. 2001, *Green. Chem.* **3**, 74.
21. Lingaiah, N., Uddin, M.A., Muto, A., Sakata, Y. 1999, *Chem. Commun.* 1657.
22. Shiraga, Y., Uddin, M.A., Muto, A., Narazaki, M., Sakata, Y., Murata, K. 1999, *Energy and Fuels.* **13**, 428.
23. Uddin, M.A., Sakata, Y., Shiraga, Y., Muto, A., Murata, K. 1999, *Ind. Engg. Chem. Res.* **38**, 1406.
24. Sakata, Y., Uddin, M.A., Muto, A., Koizumi, K., Narazaki, M., Murata, K., Kaji, M. 1996, *Polym. Recy.* **2**, 309.
25. Bhaskar, T., Matsui, T., Uddin, M.A., Kaneko, J., Muto, A., Sakata, Y. 2003, *Appl. Cat. B Env.* (In Press-APCATB 1333).
26. Bhaskar, T., Murai, K., Brebu, M., Matsui, T., Uddin, M.A., Muto, A., Sakata, Y. 2002, *Green. Chem.* **4**, 603.