

## CONVERSION OF WASTE PLASTICS TO HYDROCARBONS BY CATALYTIC ZEOLITED PYROLYSIS

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### ABSTRACT

Chemical recycling has been recognized as an ideal approach and could significantly reduce the net cost of disposal. The catalytic degradation of series of pure polymers and two samples of waste plastics over several catalysts was investigated using a designed fluidized bed reactor. Product distributions are discussed in terms of the feedstocks, catalyst structures and preliminary process models are evaluated.

### INTRODUCTION

Polymer waste can be regarded as potentially cheap source of chemicals and energy. The destruction of wastes by incineration is prevalent, but is expensive and often generates problems with unacceptable emissions. It is also undesirable to dispose of waste plastics by landfill due to high costs and poor biodegradability. Chemical recycling, i. e., conversion of waste polymers into feedstock or fuels, has been recognized as an ideal approach and could significantly reduce the net cost of disposal.

Although catalysis has been used, this often involves thermal cracking of the polymer followed by catalytic conversion of the degradation products. Most studies refer to temperatures in excess of 430°C and utilize batch or fixed-bed reactors. Problems associated with blockage and limited polymer/catalyst contact within the reactor make continuous processing and process modeling difficult in fixed-bed reactors. Recently, a fluidized-bed reactor was designed to study catalyzed degradation of polyolefins [1]. This paper considers results for the conversion of several plastics and, over a series of acid catalysts, and proposes kinetic models.

### EXPERIMENTAL

A series of the most common polymers, high density polyethylene (HDPE), polypropylene (PP), polystyrene (PS) and polyvinyl chloride (PVC), and samples of waste plastics were selected for catalytic cracking. Both pure plastics and waste plastics were pyrolyzed over acidic zeolites (HZSM-5, HMOR and HUSY), non-zeolitic ( $\text{SiO}_2\text{-Al}_2\text{O}_3$ ) catalysts and silicalite ( $\text{Si/Al} > 1000$ , siliceous analogue of ZSM-5 zeolite). Prior to use, all the catalysts were pelleted using a press (compression pressure = 160 MPa), crushed and sieved to give particle sizes ranging from 75 to 180  $\mu\text{m}$ . In general, polymer to catalyst weight ratios of 0.4:1 were used, fluidized bed reactor was at 360°C and the catalyst pellets were in the range 75-180  $\mu\text{m}$ .

A detailed description of the experimental system is given elsewhere [2] and shown schematically in Fig. 1. The reactor was an inverted bell-shaped tube (400mm long, pyrex) consisting of three sections; upper (170 × 20 mm ; i. d.), middle (30 × 10 mm ; i. d.) and lower (200 × 10 mm ; i. d.). It was heated by a three zone furnace with digital controllers and temperature read-out for each zone. Preheated nitrogen was controlled to  $\pm 1^\circ\text{C}$  and the temperature over the

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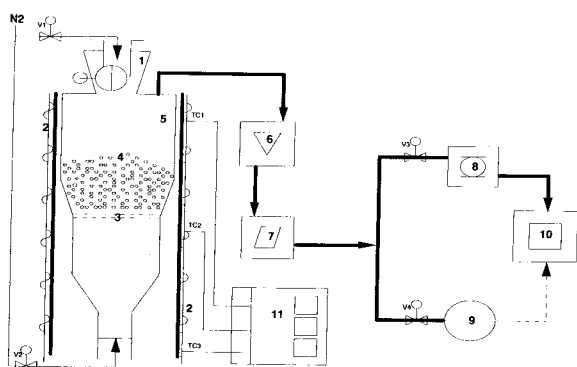


Fig. 1. Schematic Diagram of Catalytic Fluidized Bed Reactor System.

Keys: 1. Feeder 2. Furnace 3. Sintered distributor 4. Fluidized catalyst 5. Reactor 6. Condenser 7. Flow meter 8. 16-loop automated sample system 9. Gas bag 10. GC 11. Digital controller for three-zone furnace.

whole reactor varied by less than  $\pm 2^\circ\text{C}$ . Catalysts were activated by stepwise heating in nitrogen to  $520^\circ\text{C}$  and then maintained at this temperature for five hours. The polymer particles were purged under nitrogen prior to entry via a valve at the top of the reactor. Typically, products were analyzed at short time intervals and total products collected at completion.

The product collection line for the feed of PVC and waste plastics had to be somewhat modified. Because of the amount of HCl component found in the degradation product, two absorbers in series were added. Mass balances were, in most cases, greater than 90%. Residues (coke) were determined by thermogravimetric analysis (TGA). [3]

## EXPERIMENTAL RESULTS

### Degradation of polyolefins over catalysts

Table 1 summarizes the products of polyolefins (HDPE and PP) degradation over various catalysts and silicalite. The yield of volatile hydrocarbons for various catalysts (ZSM-5 > USY  $\approx$  MOR > SAHA) was much higher than for silicalite where the highest yield (nearly 95 wt%) was obtained for HZSM-5 compared to silicalite (5 wt%). Overall, the bulk of the products observed with zeolites were in the gas phase (>85 wt%) with less than 7 wt% liquid collected. The highest level of BTX were observed with ZSM-5, whilst the highest coke yields were observed with the two I2R zeolites, MOR and USY. SAHA showed the lowest conversion, USY yielded a saturate-

rich product with a wide carbon number distribution and substantial coke levels. The differences in the product distributions between the zeolites can be seen with USY producing a wider molecular weight range than ZSM-5 and MOR. Some similarities were observed between ZSM-5 and MOR with  $\text{C}_1\text{-C}_4$  and  $\text{C}_5\text{-C}_9$  yields for HDPE and PP degradation, which were approximately 60 wt% and 30 wt% respectively. However, HUSY gave the different  $\text{C}_1\text{-C}_4$  and  $\text{C}_5\text{-C}_9$  yields, which was approximately 30 wt% and 55 wt%.

### PS and PVC degradation over catalysts

The volatile products of PS degradation over various catalysts are listed on Table 2. SAHA produced more aromatic streams with large amounts of styrene. Product distributions with HZSM-5 contained more monomer materials (styrene) with over 20 wt% aromatic dimers and trimers. Comparing of the products of PS and PVC degradation over zeolites (HZSM-5, HUSY and HMOR), both HZSM-5 and HMOR gave higher yields of gases products, while HUSY yielded the very high amount of residue. The results on the feed of PS show that the larger pore structure SAHA result in aromatic selectivity, while small channels present in zeolites give resistant to aromatics. As can be seen on Table 2, the amount of residue, on the feed of PS and PVC, was more exaggerated in the case of HUSY with its larger-pore openings and internal supercages. HZSM-5 is resistant to coking when coke builds up on outersurface and the product stream remains essentially unchanged, whereas the weakness and lower density of the acid sites in SAHA along with the increased tolerance to "coke" in the larger mesopore systems provide the most likely reasons for the lack of variation in the product stream over these catalysts.

### Catalytic degradation of plastic wastes

Two samples of plastic wastes were selected from Manchester City area. One of the materials consisted of mixed cylindrical pieces of stripped plastic insulation (PW1) obtained from a dealer in scrap wire and cable. Residue strands of copper wire were removed from the plastic waste before catalytic degradation by treatment with dilute nitric acid. The other is a mixed plastic (PW2) obtained from recycling center with the component of PE ( $\sim 54$  wt%), PP ( $\sim 30$  wt%), PS ( $\sim 15$  wt%) and with 1 wt% PVC mixtures. For both of plastic wastes, catalytic degraded product was obtained as solid, liquid, and gases. As shown in Fig. 2, the main part of the solid product accumulated in the reactor, but some was also in the condenser. The liquid product was dark and vis-

Table 1. Product distributions of HDPE and PP degradation at 360°C over various catalysts

Yield (wt% feed)	ZSM-5		USY		MOR		SAHA		Silicalite	
	PE	PP	PE	PP	PE	PP	PE	PP	PE	PP
Gases (C1~C9)	93.23	94.01	89.71	90.30	88.56	87.01	84.5	86.1	4.14	5.19
Gases (C1~C4)	64.14	67.52	34.81	37.10	60.77	58.43	30.3	22.5	3.21	3.81
Gasoline(C5~C9)	27.09	25.06	53.67	52.36	27.79	28.58	54.2	63.5	0.93	1.38
Liquid	2.27	2.26	3.22	3.54	2.51	4.42	3.4	4.4	1.51	1.39
Residue	4.53	3.73	7.07	6.15	8.93	8.56	12.1	9.4	94.36	93.42
BTX	2.00	1.52	1.23	0.92	-	-	-	-	n.d.	n.d.

Liquid : condensate in condenser and captured in filter; Residue : coke and unconverted polymer; BTX : benzene, toluene and xylene; - : less than 0.01 % ; n.d. : not detectable.

Table 2. Product distributions of PS and PVC degradation at 360°C over various catalysts

Yield (wt% feed)	ZSM-5		USY		MOR		SAHA		Silicalite	
	PS	PVC	PS	PVC	PS	PVC	PS	PVC	PS	PVC
Gases	4.25	30.64	3.84	28.11	1.85	31.07	0.72	30.29	0.05	34.49
Styrene	67.52	n.d	61.54	n.d	58.52	n.d	75.45	n.d	72.12	n.d
Other aromatics	21.39	n.d	16.60	-	31.22	n.d	15.57	-	22.52	-
HCl	n.d.	54.52	n.d.	55.87	n.d.	55.52	n.d.	55.45	n.d.	56.2
Residue	6.84	14.81	18.02	16.02	8.41	13.41	8.26	14.26	5.31	9.31

- : less than 0.01 % ; n.d. : not detectable.

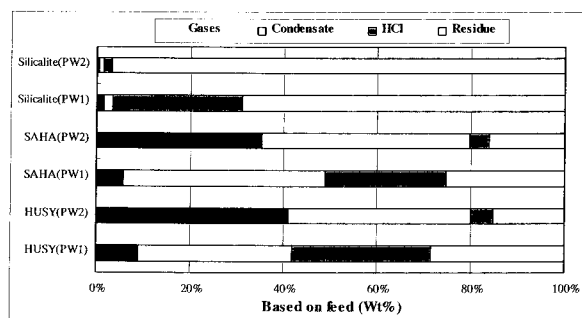


Fig. 2. Distributions of main products (wt%) for plastic mixtures of PW1 and PW2.

cous. Gases product was in the greatest part HCl, which was observed in the NaOH scrubber. Other gases components were determined by GC.

In the case of PW1, the amounts of residue and liquid obtained in the experiment were greater than from pyrolysis of pure PVC, while the amount of HCl was less, probably due to the presence of plastics other than PVC in the scrap insulation. On the basis of the HCl yield, the sample was estimated to be about 70 % PVC. The increased yield of char and of liquid and the low yield of light hydrocarbons are consistent with the effect of larger particle size in the fluidized bed. In the case of PW2, it gave a yield of and condensate of about 70.5 wt% hydrocarbon liquid.

The results obtainable by catalytic cracking of

mixed plastic waste are probably predictable from knowledge of the behavior of the pure plastics together with an understanding of the effects of process conditions on product yield and quality. Catalytic degradation of plastic waste appears to have potential as a recycling technology in which all the product of the process can be recycled as monomers or as useful hydrocarbon fuels. It also appears to be possible to remove the chlorine content of chlorinated polymers almost quantitatively by a preliminary low temperature pyrolysis step. Further research would appear to be warranted to evaluate whether reaction rates can also be predicted in mixture materials.

## KINETIC MODELING

### Kinetic aspects

It was demonstrated, using thermal analysis [4], that polymer degradation can be represented as

$$\frac{dW_p}{dt} = A_p \times e^{E_a/RT} \times (W_p)^{n_p} \times \eta_c \quad (1)$$

where p refers to polymer and c to coke.  $A_p$  and  $n_p$  are the frequency factor and order of reaction for the polymer degradation and  $\eta_c$  is defined as the rate of degradation over a coked catalyst relative to that over a fresh catalyst. Simulation of the

process facilitated determination of the parameters. For example, degradation of HDPE over USY gave  $A_p = 3.5 \times 10^{10} \text{ s}^{-1}$ ,  $n_p = 2$  and  $E_a = 103 \text{ kJ mol}^{-1}$ . For the coking process,  $E_a = 8.7 \text{ kJ mol}^{-1}$ , reaction order was zero and the frequency factor was  $0.7 \text{ s}^{-1}$ .

SEM studies[5] using a heated stage indicate that, for premixed polymer/catalyst particles, at temperatures around  $300^\circ\text{C}$ , the molten polymer is drawn into the spaces between particles and hence to active sites on the external surface of zeolite catalysts or in larger pores of amorphous materials. Surface reaction then produces lower molecular weight materials which, if sufficiently volatile at reaction temperature, can either diffuse through the polymer film, as products, or react further in the pores, including micropores, of zeolites. As a result, product distributions reflect features of the zeolite catalysts in relation to their pore systems and chemical composition. This is evident in the product distributions shown on Tables 1 and 2. The results indicate that although the initial cracking of HDPE must be confined to the external surface and pore mouths of the zeolite catalysts, the resultant initial cracked products are then degraded within the zeolite, since the product distributions are significantly influenced by the structure of particular zeolite.

#### The model

The benefit of experimental studies has been the improvement of the catalyst; nevertheless, there are still important gaps in aspects relevant to the further development of a process. Of these, kinetic modeling should be singled out, as it is necessary for reactor design at an industrial scale. An important challenge in the process modeling effort is the development of reliable kinetic equations for processes with complex feedstocks.

It is well known that the acid-catalyzed hydrocarbon reactions are involved in cracking macromolecules proceed via carbenium ion intermediates. [6-8] The formation of carbonium and carbenium ions and their reaction behaviours play an important role in the reaction. However, papers concerning the kinetic modeling of catalytic processes for polymer degradation have great limitations, which are shared with the study of other complex reaction schemes such as catalytic cracking, and reforming. The literature available involving the mechanistic considerations with carbenium ion chemistry for polymer degradation catalyzed by catalysts is rather scarce. [9,10] A newly kinetic/mechanistic model is proposed, and for use to study the catalytic degradation of polymers and in attempt to optimize the potential benefit of catalytic polymer recycling. The model including

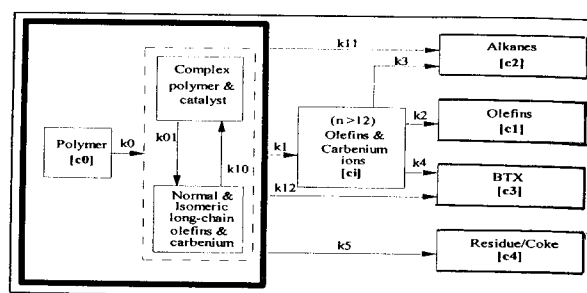


Fig. 3. A mechanistic and kinetic scheme representing polymer degradation over acid catalysts.

the main mechanistic features and kinetic reaction schemes for polymer degradation to observed products over cracking catalysts was investigated (Fig. 3).

- Liquid-phase polymer: initially, solid polymer is freely dropped into the reactor and immediately melts to disperse around the catalysts. The molten polymer, in contact with the catalyst particle forms a polymer/zeolite complex, reaction commencing at the surface.
- Olefins and intermediate precursors for carbenium ions. The carbenium ions rapidly reach a steady-state concentration. Alkanes may be generated, via hydrogen transfer, and initially will be largely long-chain products. The number of active sites limits the number of carbenium ions.
- Evolution of products: once the intermediates are produced, further reactions could be expected to produce smaller chain olefins at equilibrium with surface carbenium ions as well as alkanes, BTX and coke. The equilibrium mixture of olefins and carbenium ions subsequently reacts further (hydrogen transfer, cracking to gases, olefins desorption) to produce the final products.

On the basis of the above reaction pathway, a set of differential equations were developed and numerically integrated by a fourth-order Runge-Kutta algorithm with Matlab (Version 4.2) to find the individual rate constants by minimizing the sum of the squared deviations between calculated and experimental results. A typical result for catalytic conversion of high density polyethylene over HUSY is shown in Fig. 4. The model gave a good representation of experiment results. In this work, a kinetic/mechanistic model giving chemical information, applicable to the fluidized-bed reactions, has been developed. This model takes into account mechanistic considerations in relation to chemical composition (alkanes, olefins, aromatics and coke) and catalyst deactivation for the chemical reactions that occurred in the catalytic degradation of polymers. These materials (alkanes,

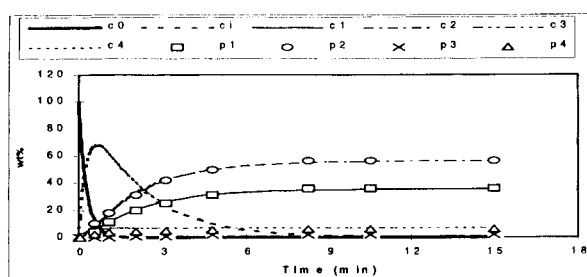


Fig. 4. Calculated and experimental results for the degradation of HDPE over HUSY. c: model, p: experimental data. 0: unconverted polymer, i: intermediates, 1: olefins, 2: alkanes, 3: BTX, 4: residue/coke.

olefins etc.) are present in various molecular weight ranges and, consequently, can be used to define lumps based on the chemical behavior of each group, and to account for chemical reactions. The kinetic rate constants, representing chemical reactions between lumps, are then no longer purely empirical but they represent the overall kinetics of the possible reactions in the lumped components. Reaction products are largely determined by carbenium ion chemistry (isomerization, C-C bond scission, H-transfer, oligomerization/alkylation) which is influenced by acid-site strength, density and distribution and also by pore/cage effects. A fuller model is being developed from mechanistic paths which will take into account the different reacting conditions and the behaviors of catalyst deactivation as related to the structure of catalysts and their acid sites.

## CONCLUSIONS

Plastics were pyrolyzed over catalysts using a specially developed fluidized bed. The catalytic degradation of plastics performed in fluidized bed reactor was thus found to be a useful method for the production of potentially valuable hydrocarbons. The systematic experiments carried out with several catalysts show that under appropriate reaction conditions, catalysts may be selected to reduce the required reaction temperature, improve the yield of volatile products, and provide selectivity in the product distributions. A kinetic/mechanistic model giving chemical information, applicable to the fluidized-bed reactions, was used to predict production rates and product selectivity for the catalytic degradation of polymers. The model gave a good representation of experiment results. The model based on a reaction scheme for the observed products and catalyst deactivation in relation to chemistry has been developed.

This paper outlines some recent results relevant to the conversion of polymers to chemical feedstocks and fuels using various catalysts and also attempts to provide a framework for understanding the variety of influences on product distribution.

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## 催化裂解轉化廢塑膠為碳氫化合物

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**關鍵詞：** 催化裂解；高分子化合物；流體化床反應器；高分子化合物；沸石

### 摘 要

化學反應回收廢塑膠成為有價值之碳氫化合物，不僅是固廢能源再生處理的理想方式，同時也可以大大降低塑膠廢棄處理所需的成本花費總值。本文章使用流體化床反應器來研究催化裂解各別單一塑膠及混合廢塑膠樣品，分解成為可利用之小分子碳氫化合物；除探討進料種類、催化劑結構對於產物分佈情形之影響外，並提出催化裂解程序模型來推導相關反應動力資料以供製程放大。

