

Dehydrogenation of Methylcyclohexane Over Pt Supported on HY-zeolite, Alumina and Composite of HY-zeolite and Alumina Catalysts

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ABSTRACT

0.35 wt.% Pt supported over HY zeolite, γ -alumina and a mixture of HY+ γ Al₂O₃, have been used as catalysts for methylcyclohexane (MCH) conversion. The catalytic activity tests have been carried out using a pulse technique method under atmospheric pressure at reaction temperatures varying between 200° and 500°C.

The results revealed that, at lower reaction temperatures (200-400°C), methylcyclohexane has been partially isomerized to dimethylcyclopentanes and ethylcyclopentane. Upon raising the temperature, cracking and dehydrogenation reactions are predominated and the converted products consist mainly of paraffinic gases and aromatics. The highest values of toluene yield can be obtained at 500°C, at which 44.2 wt.%, 31.5 wt% and 11.25 wt.% of this component are produced on using Pt/Al₂O₃, HY+Al₂O₃ and HY catalysts, respectively.

INTRODUCTION

Aromatic hydrocarbons have the highest octane number and are considered the chief octane upgrading compounds for petroleum naphtha stocks (1). They are produced primarily by catalytic reforming in which the most predominant reaction is dehydrogenation of naphthenes (2). The dehydrogenation of methylcyclohexane (MCH) to toluene is representative of one of the major types of reactions occurring in this process (3). A typical aromatic composition in a reformed product consists of 10% benzene, 47% toluene, 32% xylenes and 11% remainders (4).

Toluene contributes effectively to the antiknock characteristics of paraffinic-base or other base stock and assigned a high blending octane number. It is prized for its combination of high octane number and suitable volatility. Besides, toluene is much in demand as feed stock for chemical manufacture such as benzene, phenol, caprolactum, benzoic acid, benzyl derivatives, saccharin, medicines, dyes and perfumes. It is also a source of polyurethanes resins, detergents and scintillation counter. Toluene can be used as a solvent for paints and coatings, gums, resins, most oils, rubber, vinyl organosols and as a diluent and thinner in nitrocellulose lacquers. It acts as an adhesive solvent in plastic toys and model airplanes and several other purposes (5).

The dehydrogenation of cyclohexanes to aromatics occurs readily in the presence of dual functional catalysts (6-8). This reaction is rapid and highly endothermic (9). It is favored by high temperature (10,11) and low pressure.

In this study, the catalytic activity of Pt supported on three various supports namely, HY zeolite, γ -alumina and a mixture of HY and γ - Al_2O_3 has been investigated through the dehydrogenation of methylcyclohexane. The effect of reaction temperature on the distribution of the converted products is also evaluated.

EXPERIMENTAL

I) Feed and catalyst supports:-

- 1- Methylcyclohexane (MCH) : Panreac (Montplet and Esteban-Sa)
- 2- Na-Y zeolite (Davison, SMR-6-1030)
- 3- γ -alumina (supplied by Frensh Institute of Petroleum)

II) Catalysts preparation⁽¹²⁾ :

HY zeolite has been prepared from its cation form by ion exchange using NH_4Cl solution followed by calcination at 530°C for 4 h.

HY, Al_2O_3 and HY+ Al_2O_3 were impregnated with an aqueous solution containing the requisite quantities of chloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) in order to get catalysts containing 0.35 wt.% Pt on each support. The catalysts were dried, calcined and then reduced in the catalytic reactor in situ in a flow of H_2 gas before carrying out the hydroconversion experiments.

III) Apparatus ^(13,14)

The behavior of the prepared catalysts towards MCH hydroconversion at various reaction temperatures and atmospheric pressure has been studied using the pulse technique. The apparatus composed of a microcatalytic reactor directly attached to the injection part of a gas chromatographic apparatus, model (PERKIN-ELMER) fitted with a flame ionization detector (FID) and electronic recorder to provide a rapid analysis of the reactant effluents. Figure (1). The micro-reactor was made from a stainless steel tube of 12cm length and 3.5 mm internal diameter and placed in a tube furnace.

The reactor temperature was measured and recorded via a thermocouple. Silicon oil chromatographic column was employed.

Procedure ⁽¹³⁾:

0.1gm portion of the fresh catalyst under investigation was charged in the middle zone of the reactor. The catalyst was activated for 2 hrs at 400°C in a stream of nitrogen gas. The temperature was then raised stepwise to the desired reaction temperature.

A dose of 10^{-3} ml of the reactant was injected into the reactor. The chromatographic column receiving the reaction effluents was maintained at constant temperature (70°C). Direct comparison between the reaction products and the feed was accomplished by injecting two similar pulses of reactants in the same reactor with and without catalysts, under identical conditions, respectively. The comparison of both pulses directly gives the conversion.

RESULTS AND DISCUSSION

The catalytic hydroconversion of methylcyclohexane (MCH) was carried out at different reaction temperature (from 200° to 500°C) and at atmospheric pressure using the pulse method.

Three types of catalysts, namely. 0.35 wt% Pt/HY, 0.35 wt% Pt/Al₂O₃ and a mixture of 0.35 wt % Pt/HY+Al₂O₃, were employed in this study.

I. 0.35 wt% Pt/HY catalyst:-

The effect of reaction temperatures on the distribution of reaction products through the hydroconversion of MCH using 0.35 wt% Pt/HY catalyst are illustrated in Table (1) and Fig. (2).

The total conversion of MCH is 11 wt% at 200°C and increases to 94.2 wt% at 500°C.

The isomerization reaction enhances with increasing the reaction temperature, and the highest concentration of dimethylcyclopentanes isomers (DMCPs) 29.2wt% can be obtained at 400°C. At higher temperatures, the lighter hydrocarbons are predominated in the product due to prevalence of cracking reaction.

The catalytic hydroconversion of MCH gives 7 wt% of hydrocracked product at 200°C whereas at higher temperature (i.e 500°C), the lighter products increase drastically to arrive 71.4 wt%.

Pt/HY catalyst exhibits a low activity towards dehydrogenation of MCH to the corresponding aromatic. The maximum value for toluene produced at 500°C, amounts to 11.25 wt% only.

II 0.35 wt% Pt/Al₂O₃ catalyst

Table (2) and Fig (3) show the hydroconversion results of MCH on Pt/ γ Al₂O₃ supports as a function of reaction temperatures.

Pt/ γ Al₂O₃ catalyst shows a lower activity than Pt/HY catalyst, at the same condition due to the difference in acidity (15-19) and surface area. The converted product increases from 17.6 wt% to 70.72wt% upon raising the temperature from 250° to 500°C.

The maximum isomers weight in the product yield (17.1wt%) is achieved at 400°C and composed mainly of dimethylcyclopentanes (DiMCPs) and ethylcyclopentane (ECP) (20).

Comparing the data in Tables (1) and (2) shows that ECP appears upon using Al₂O₃ support in an appreciable amount (close to 10.5 wt% at 400°C), but this component is completely absent in case of HY zeolite. This may be attributed to the wider pore diameter of alumina than zeolite which permits the formation of ECP molecule, also permits its diffusion out of the catalyst.

Dehydrogenation of MCH, is the major reaction taking place over Pt/Al₂O₃ catalyst. The percentage of aromatics content produced increases from 7.5 to 44.2wt% as the temperature increases from 250° to 500°C. Aromatics are composed mainly of toluene.

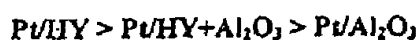
The total hydrocracked products are low compared to those given by Pt/HY catalyst due to the higher acid site strength of HY zeolite.

Fig (3) shows that, increasing the temperature from 250 to 500°C led to a high increase of the cracked product from 1.3 to 18.5 wt%.

III 0.35 wt% Pt/HY+Al₂O₃:

The data are illustrated in Fig. (4) and Table (3). Pt loaded on a mixture of 50% HY+ 50% Al₂O₃ support has an intermediate hydroconversion activity between those of Pt/HY and Pt/Al₂O₃ catalysts. The total conversion increases gradually from 1.6 to 67.6 wt% upon raising the reaction temperature from 200 to 500°C.

The isomerization reaction enhances with temperature up to 400°C at which 21.3 wt% of isomers can be obtained. The isomers composed mainly of DMCPs and some ECP. Beyond 400°C, a considerable suppression of the isomerization activity has occurred due to ascendancy of the rate of cracking reaction at elevated temperatures. By comparing the results of Table (3) with those of Tables (1) and (2), it is obvious that, the isomerization activity of the investigated catalysts can be arranged as follows:-



Pt/HY+Al₂O₃ catalyst shows a moderate efficiency towards the dehydrogenation reactions. Its capability of transforming MCH to toluene is higher than Pt/HY, but lower than Pt/ Al₂O₃ catalysts. The aromatic concentration increases from 1.6 to 31.5 wt% with increasing the reaction temperature from 200 to 500°C.

Since cracking is considered to be an endothermic reaction, it proceeds preferentially at higher temperatures, Where as only 2.5 wt% of the cracked products are produced at 250°C, an appreciable increase in this value to become 25.9wt% of lighter constituents is achieved at 500°C.

REFERENCES

1. 17th World Petroleum Congress, Rio de Janeiro, 1-5 September, (2002).
2. D.W. Penner, "The role of Aromatics and Catalytic Reforming in The 2000⁺ Refinery", Erlangen, Germany, (1999).
3. John H. Sinfelt. *Journal of Molecular Catalysis A: Chemical*, Vol. 163, Iss. 1-2, 4 Dec. p.123-128. (2000).
4. Charles, N. Satterfield, *Chem. Eng. Ser.*, New York, McGraw-Hill Book Com., p. 240, (1980).
5. Bahl. B.S.; Bahl, A, *Advanced Organic Chemistry* S chand and Company Ltd, ram najor. New-Delhi, India second edition p.925, (1983).
6. Smirniotis, P.G., and Wenmin Zhang *Ind. Eng. Chem. Res.*, 35, p.3055-3099. (1996).
7. Simirniotis, P.G., Ruckenstein, E. *J. Catal.*, 140, 526-542. (1993a).
8. Simirniotis, P.G., Puckenstein, E. *Catal. Lett.*, 25, p.351-359. (1994c).
9. Yongsunthon. I; *Alpay-E/ Chemical Engineering Science*. V 55 n 23 Dec., p.5643-5656, (2000).
10. Kariya Nobuko; Fukouka Atsushi; Utagawa Tadashi; Sakuramoto Masashi; Goto Yasushi; Ichikawa Masaru. *Appl. Catal. A: General*. V 247 n 2 Jul 25, p. 247-259. (2003).
11. Kariya-Nobuok; Fukuoka-Atsushi; Ichikawa Masaru. *Appl. Catal. A: General* v. 233n 1-2 Jul 10, p. 91-102. (2002).
12. Mohamed, L.Kh. Ph.D Thesis, Faculty of Engineering, Cairo University (2000).
13. Mohamed, L. Kh., M.Sc. Thesis, Faculty of Engineering, Cairo University (1992).
14. *Catalysis Review* Vol. 8, p. 175-185, (1987).
15. Caster, Ph. D. Thesis, University of Wisconsin- Milwaukee, (1995).
16. Y. Hong, Ph.D. Thesis, University of Wisconsin-Milwaukee, (1995).
17. V. Gruver and J.J. Fripiat, *J. Phys. Chem.*, 98, (1994).
18. El-Khatib, S.A. Mohamed, L.Kh., and Hassan, H.A., *J. Eryp. Soc. Eng.*, Vol. 31. No. 3, p.38. (1992).
19. El-Khatib, S.A. Mohamed, L.Kh., and Hassan, H.A., *J. Eryp. Soc. Eng.*, Vol. 31. No. 4, p.89. (1992).
20. Roger E. Leveque, *Anal. Chem.*, Vol. 39, No. 14, p. 1811-1818. (1967).

**Table (1) Effect of reaction temperature on the hydroconversion of MCH
Using Pt/HY catalyst**

Type of reaction	200	250	300	350	400	450	500
Cracking	7	15.1	27.5	40.5	45	57.5	71.35
Isomers	3.1	9.61	13.23	20.11	29.15	19.2	11.6
Toluene	0.9	2.9	5	5.95	7.9	9.95	11.25
Conversion	11	27.61	45.73	66.56	82.05	86.65	94.2

**Table (2) Effect of reaction temperature on the hydroconversion of MCH
Using Pt/ γ -Al₂O₃ catalyst**

Type of reaction	200	250	300	350	400	450	500
Cracking	---	1.3	5.1	7.3	10.04	11.78	18.54
Isomers	---	8.77	11.37	15.9	17.07	15.75	7.98
Toluene	---	7.53	18.23	22.71	30.08	35.1	44.2
Conversion	---	17.6	34.7	45.95	57.19	63.63	70.72

**Table (3) Effect of reaction temperature on the hydroconversion of MCH
Using Pt/HY+ γ -Al₂O₃ catalyst**

Type of reaction	200	250	300	350	400	450	500
Cracking	---	2.5	8.34	12.29	15.29	20.95	25.9
Isomers	---	3.68	8	10.19	21.29	14.68	10.2
Toluene	1.57	12.51	23.36	24.8	26.39	28.65	31.5
Conversion	1.57	18.69	39.7	47.28	62.97	64.28	67.6

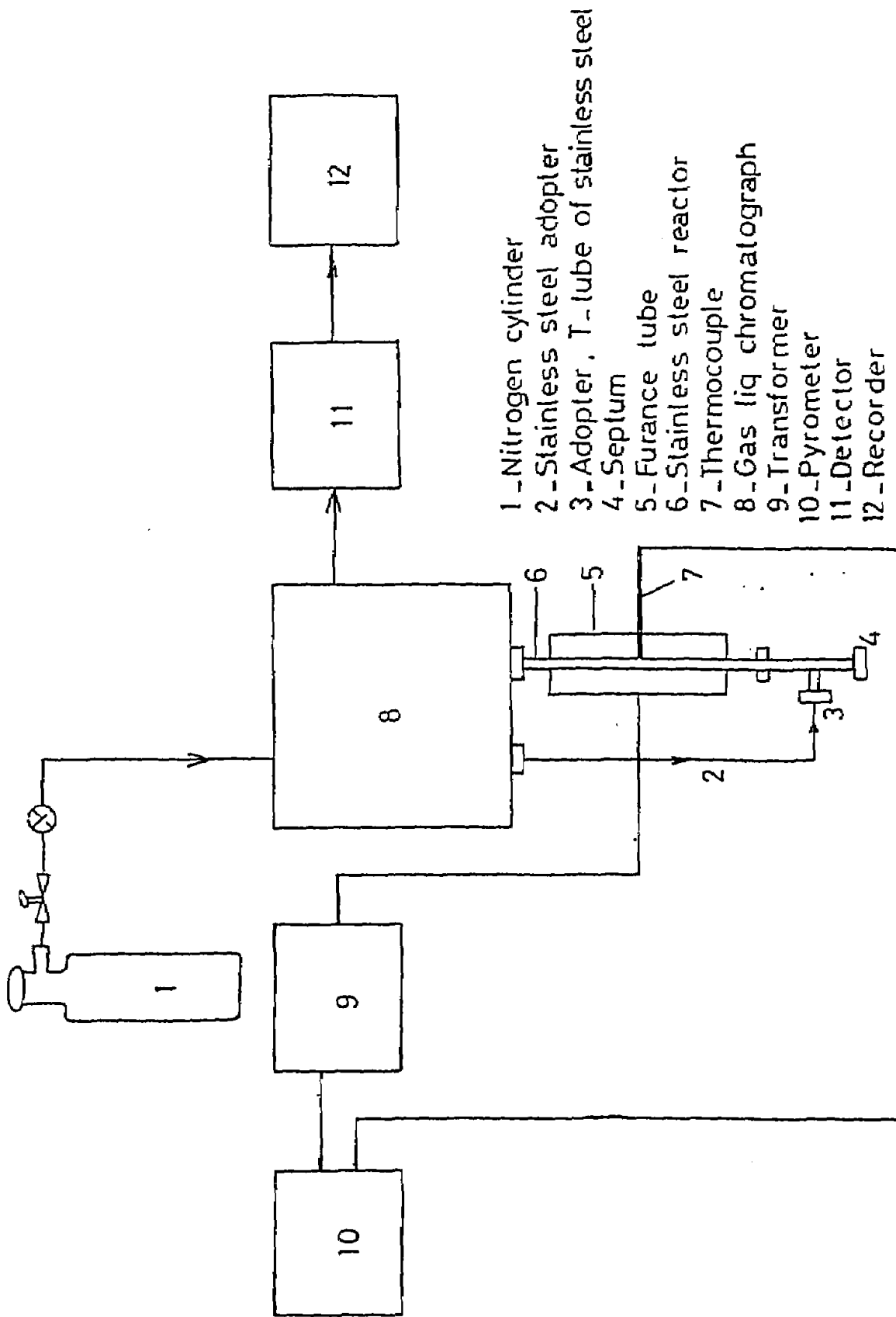


Fig.(1) : Pulse Microcatalytic unit .

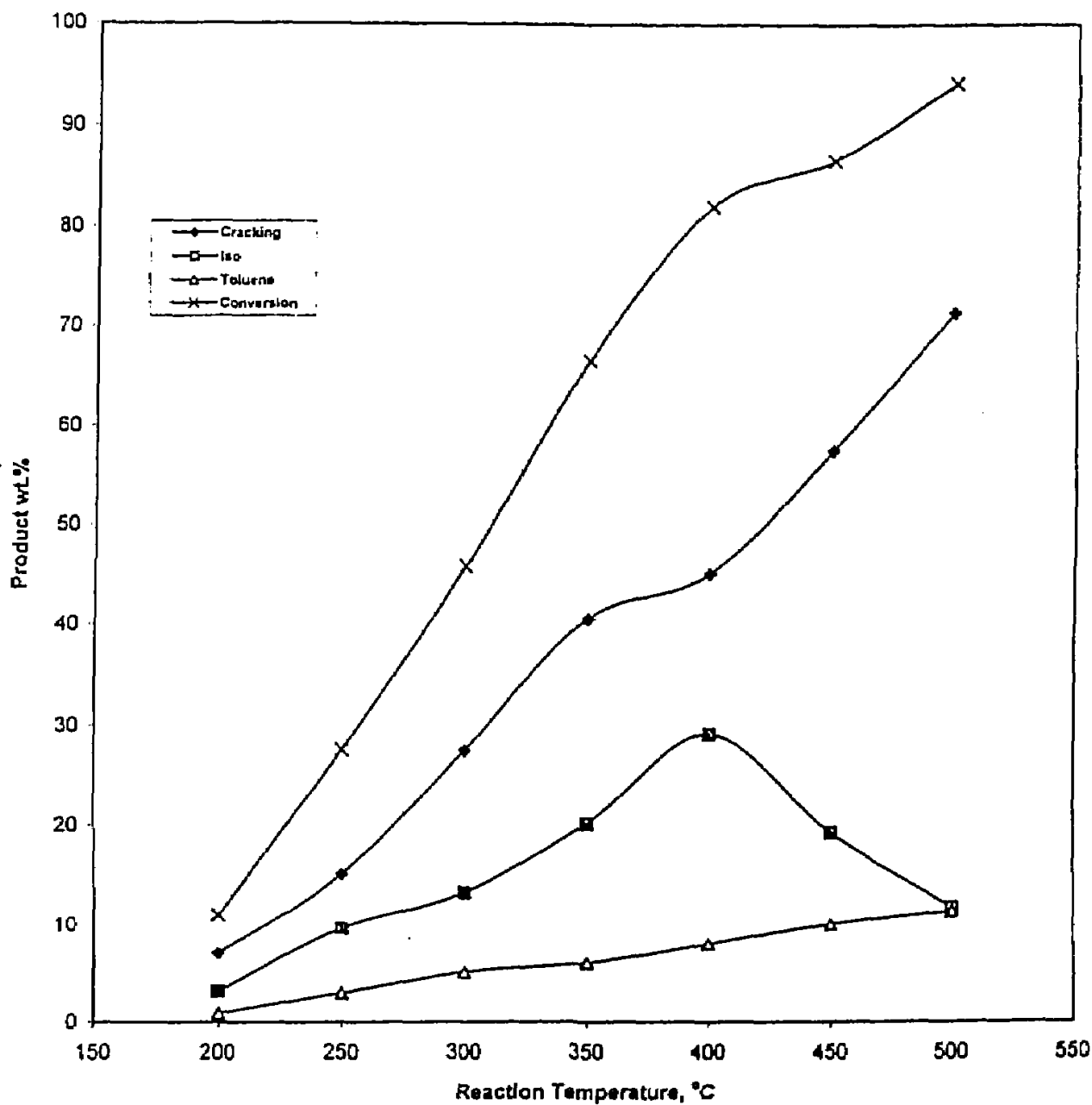


Fig. (2) Distribution of reaction products of MCH hydroconversion at different reaction temperatures, using Pt/HY Catalyst

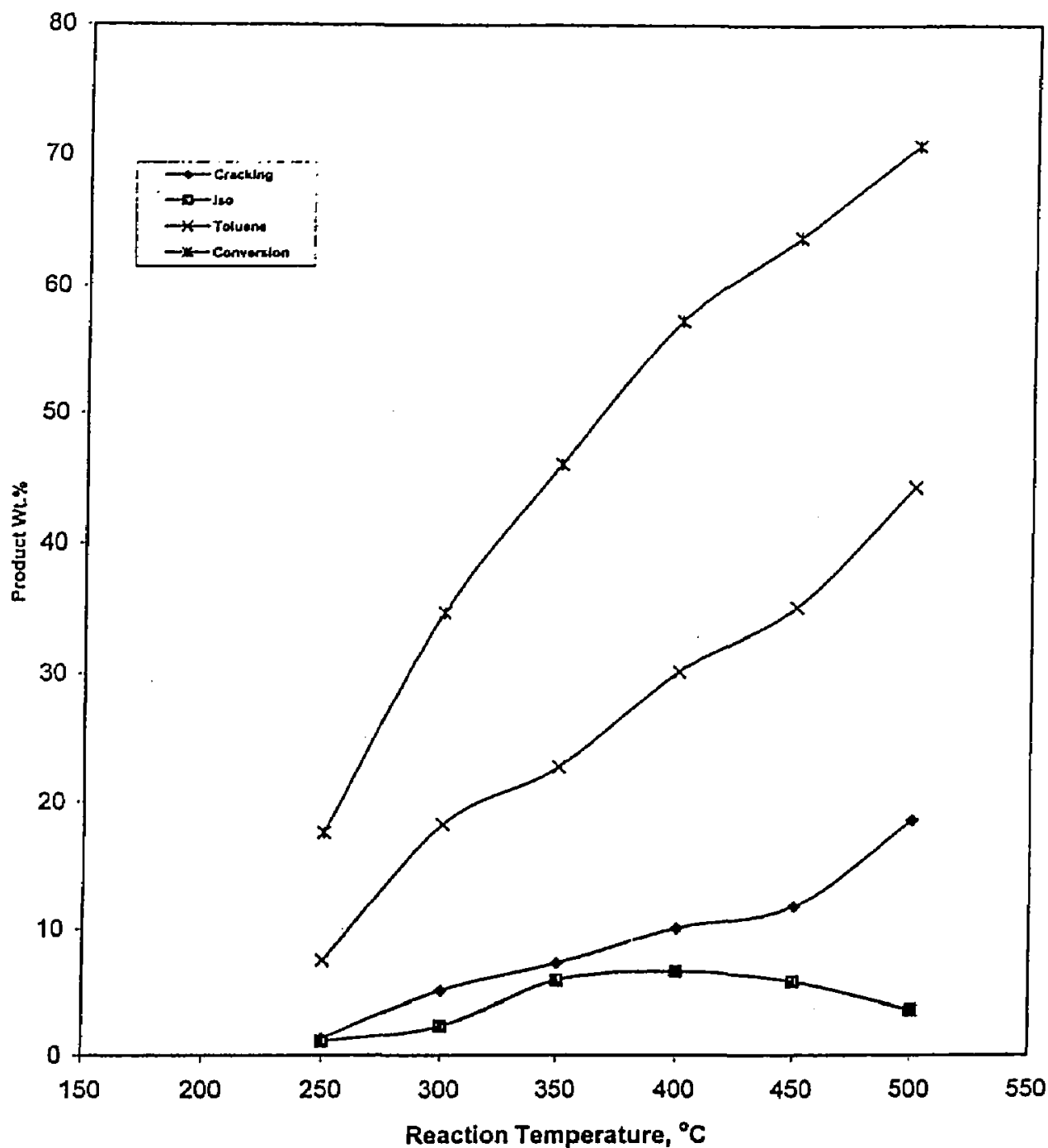


Fig. (3) Distribution of reaction products of MCH hydroconversion at different reaction temperatures, using Pt/ γ -Al₂O₃ Catalyst

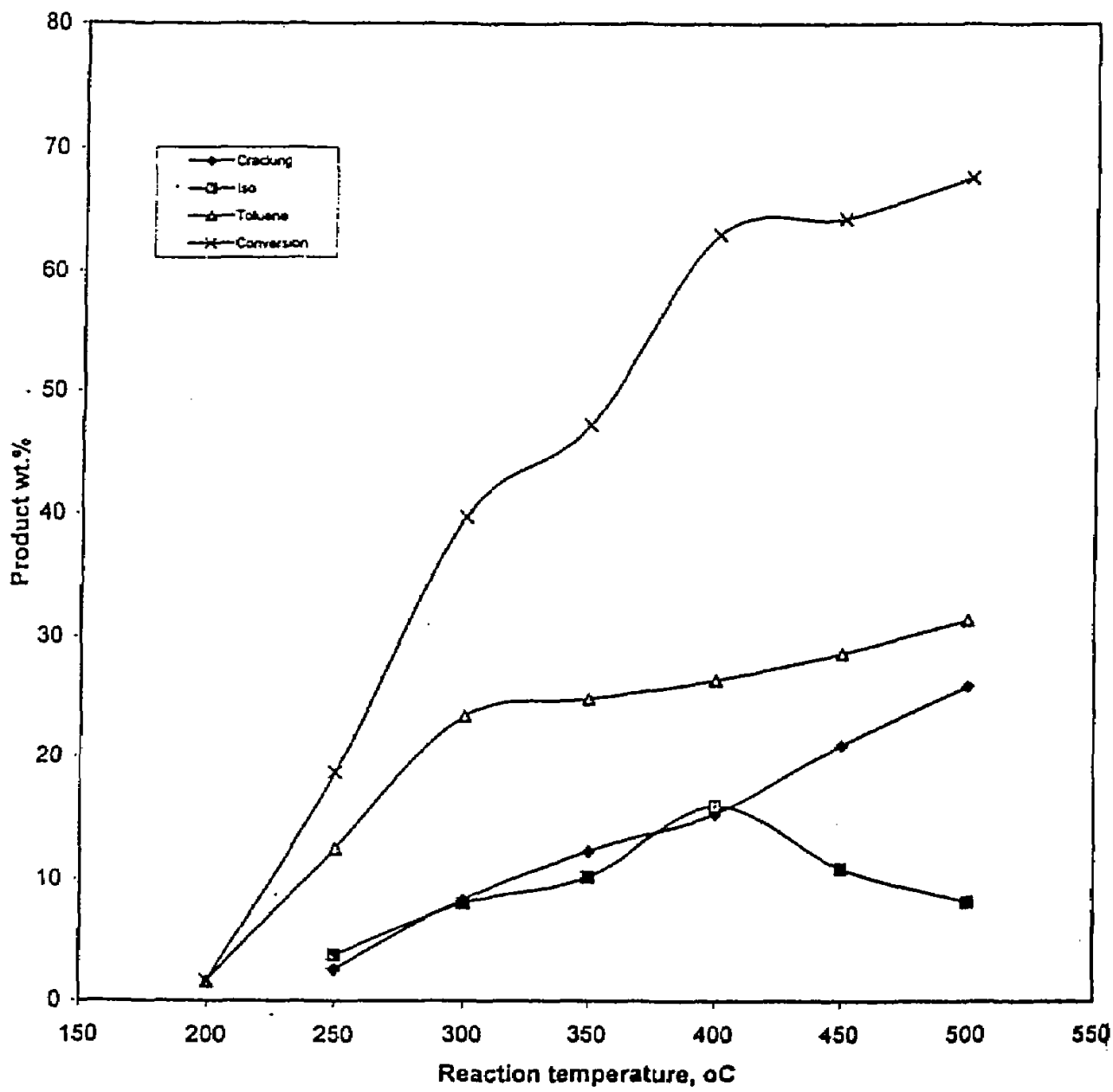


Fig. (4) Distribution of reaction products of MCH hydroconversion at different reaction temperatures, using Pt/HY+ γ -Al₂O₃ Catalyst