Thermolysis and Hydrogenolysis of Polyethylene under Steam Pressure

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Synopsis

Thermolysis and hydrogenolysis of polyethylene under steam pressure were carried out by batchwise autoclave in the recovery of liquid petrochemical resources from waste polymers. Thermolysis of polyethylene under steam pressure occurred in the temperature range 400–475°C and reaction pressures up to 213 bar. The presence of steam is advantageous for an increase in liquid products and 450°C is an appropriate temperature for the formation of low molecular aromatic compounds. Hydrogenolysis of polyethylene was studied at 450°C and initial hydrogen pressure range of 10–100 bar under steam pressure. Over 80 wt % of the low-boiling product was converted to saturated hydrocarbons at 40 bar hydrogen pressure, which corresponds to 1 mole hydrogen to 1 mole monomeric unit of polyethylene. The schemes for the thermolysis and the hydrogenolysis, especially the aromatization, are discussed.

INTRODUCTION

The present investigation was undertaken to recover useful hydrocarbons by thermolysis and hydrogenolysis of polymers in the presence of steam (water). The reasons for the intentional addition of steam are as follows: If this process can be scaled up to a large continuous plant, the heating of the reactor can be more uniform, that is, the process control can be easier by blowing superheated steam. Steam distillation can be combined to separate the liquid product. The presence of steam prevents dangerous accidents from the leakage of a combustible substance (high-pressure hydrogen in hydrogenolysis). In addition, since a high reaction temperature preferentially forms aromatic compounds in the decomposition of petroleum hydrocarbons, it is possible that the reaction condition favorable for the aromatics production can be obtained by the retardation of the excess decomposition of polymers owing to steam pressure. The object of this report is to obtain fundamental data for this process.

The experiments were carried out in a rotating autoclave at pressures of 155–410 bar (reaction pressures generated by steam and 10–100 bar initial hydrogen pressure in hydrogenolysis) and temperatures of 400–475°C, without catalyst (ferric oxide was used in some experiments). Experimental conditions on the thermolysis and the hydrogenolysis of polyethylene for the purpose of producing liquid fractions were studied.

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EXPERIMENTAL

Equipment and Materials

Experimental runs were made in a 890-cm^3 stainless steel autoclave, which was self-sealed by a Bridgman-type copper gasket. The autoclave was fitted with two external heating mantles connected to an automatic-temperature-controlling instrument through a thermocouple. The polymers were mixed by rotating the autoclave, aided by the presence of steel balls. A chromel–alumel thermocouple inserted in a thermocouple well at the center of the autoclave allowed for temperature control and recording.

The materials used in this study were polyethylene (PE) pellets without added antioxidant (Sumikathene F101-1, manufactured by Sumitomo Chemical Co. Ltd.). The PE had a density of 0.924 g/cm^3, a melting point of 112°C, a weight-average molecular weight of 4.45 × 10^5, and a melt index of 0.3.

Operating Techniques

The desired amounts of PE and water (unless otherwise stated, 30 g PE + 60 g water) were added to the autoclave and then deaerated by bubbling nitrogen and hydrogen in the case of thermolysis and hydrogenolysis, respectively. The autoclave was heated slowly up to 300°C in order to minimize the temperature gradient owing to the thickness of the autoclave. The heating unit was operated at maximum capacity above 300°C. At the time when the autoclave temperature reached the desired level, the experimental run was considered to start. The preheating period at 400°C equaled approximately 4 hr, and at 450°C, approximately 4.5 hr.

After the experimental run, the external heating mantles were removed, the autoclave was cooled quickly to room temperature, and then the product was analyzed.

Because of the uncertainty of the measurement of the absolute volume of the gaseous products, the elevation at the end of the reaction was defined as the yields of the gaseous product, and the composition of the products was represented by the molar ratio to methane. The gaseous product was analyzed by vapor phase chromatography (VPC) connected directly to the autoclave. A 2-m × 3-mm steel column packed with a squalane or molecular sieve 13X(s) was used and operated isothermally at 37°C.

The yields of total hydrocarbon and the low-boiling product (<100°C, abbreviated as LBP below) in it were measured as liquid products. A structural group analysis (saturated hydrocarbons, olefins, and aromatics) of LBP was performed using the method of fluorescent indicator adsorption (FIA).[1] The FIA apparatus was packed with FIA-grade silica gel prepared by Merk Co., and isopropanol was used as an eluent. Liquid products (LBP) were also analyzed qualitatively and quantitatively by the combined use of VPC and IR spectrum measurements. The high-boiling product (>100°C) was not analyzed in this study.

RESULTS AND DISCUSSION

Thermolysis

Experimental conditions and results of the thermolysis under steam pressure are listed in Table I. The liquid product was inflammable, dark brown in color, and had an odor like gasoline. The higher the reaction temperature, the darker the product was. It depended on the precipitation of the carbon particle by excess decomposition. Regarding the liquefaction phenomena, the maximum yield of the liquid product was obtained at 400°C at 4 hr. A fair amount of solid residue was observed at insufficient reaction time. From the consideration of these time dependences, this process can be represented by the successive reaction from solid to liquid to gas.

The thermolysis of PE proceeds by the random scission of the main polymer chain, and chain depolymerization scarcely occurs. Therefore, the molecular weight of PE should decrease successively with the progress of thermolysis. In this batchwise experiment, cooling is required for each experimental run in order to learn the physical property of the sample. It is no anomalous conclusion that the mechanism of the thermolysis of PE is a series of successive reactions. Although the thermolysis over 400°C has been considered to be the same scheme, these features were not observed. The reason for this unfavorable phenomena is that the thermolysis proceeds effectively during a long period of preheating because of a technical problem of the apparatus (see Experimental section).

At 450 and 475°C, the time dependence of the process was expressed through a liquid–gas process; therefore, we applied the following equation to the thermolysis process and calculated the values of k and n:

$$-dW/dt = kW^n$$

where W represents the weight of liquid product at the time t:

$$-dW/dt = 1.25 \times 10^{-3}W^{3.27} \qquad 450°C$$

$$-dW/dt = 3.31 \times 10^{-2}W^{3.29} \qquad 475°C$$

Gaseous products were identified as methane, ethane, propane, n-butane, isobutane, butene-1, butene-2, and some C_5 fractions. The effect of reaction conditions on the molar ratio of each component to methane is shown in Table II. The values of these ratios decrease with increasing reaction temperature and time, which means that thermolysis is more advanced. However, a slight reverse tendency was observed on the yield of isobutane. The thermolysis reaction initiates with the formation of a free radical, and this radical participates in the propagation of the thermolysis.[2] Since the radical stability is in the order of primary, secondary, and tertiary hydrocarbons, the branched hydrocarbon was not as effective in the thermolysis process as the linear hydrocarbons.

From the data of FIA analysis of LBP, the saturated hydrocarbons (paraffins and naphthenes) increased, while olefins decreased with reaction time. Since the aromatic fraction identified by FIA includes the diene fraction, an accurate estimate was calculated by VPC analysis or by the combined analysis of VPC and IR. In the results, benzene and toluene (xylene in a special case) were identified and found to increase with reaction time (maximum wt % to LBP: toluene 15.71, benzene 5.76).

TABLE I

Experimental Conditions and Results of Thermolysis Under Steam Pressure

| Reaction conditions | | | Product | | | | Analysis of LBP | | | | | |
| | | | | Liquid, wt % | | | FIA, vol % | | | VPC, wt % | | |
Temp., °C	Pressure, bar	Time, hr	Gaseous, bar	Total	LBP	Solid wt %	Aromatics	Olefins	Saturated hydrocarbons	Benzene	Methyl cyclohexane	Toluene
400	155	0	0.0	—	—	100.0						
		2	1.5	—	—	80.0						
		4	1.7	75.7	22.6	0.0	27.6	41.1	31.3			
		6	2.5	66.2	17.1	0.0						
		8	2.8	70.8	23.5	0.0	13.0	34.9	52.1			
425	165	0	1.4	—	—	57.0[a]						
		2	4.3	61.3	29.4	0.0	20.5	33.3	46.2			
		4	6.3	51.0	26.9	0.0	23.5	25.0	51.5			
450	186	0	4.0	64.7	21.9	0.0	19.5	41.6	38.9	1.37	3.51	4.98
		2	9.3	26.8	13.2	0.0	40.6	16.7	42.7	1.96	4.26	15.43
		3	9.8	27.1	14.8	0.0	46.7	8.5	44.8	4.48	2.89	15.01
		4	10.6	23.3	9.9	0.0	48.5	10.9	40.6	5.76	5.11	15.71
		6	11.7	18.8	—	0.0						
475	213	0	7.7	35.9	18.3	0.0						
		2	16.3	7.0	—	0.0						
		4	16.3	4.2	—	0.0						

[a] Greasy substance.

TABLE II

Molar Ratio of C_2–C_4 Gaseous Products to Methane in Thermolysis Under Steam Pressure

Reaction condition		Time, hr	C_2H_6	C_3H_8	n-C_4H_{10}	i-C_4H_{10}	Butene-1	Butene-2
Temp., °C	Pressure, bar							
400	155	0	—	—	—	—	—	—
		2	1.45	1.69	0.68	trace	0.23	0.09
		4	1.84	2.65	0.98	trace	0.30	0.11
425	165	0	1.42	2.11	0.76	trace	0.34	0.09
		2	1.42	1.31	0.45	0.02	0.08	0.06
		4	0.98	0.85	0.27	0.02	0.03	0.04
450	186	0	1.06	1.17	0.30	0.01	0.11	0.05
		2	0.90	0.65	0.23	0.03	0.02	0.03
		4	1.01	0.66	0.11	0.03	trace	
475	213	0	0.86	0.64	0.17	0.02	0.02	0.02
		2	0.63	0.40	0.06	0.04	—	0.01
		4	0.63	0.38	0.06	0.04	—	0.01

Although the thermolysis of PE for processing industrial waste was reported by Ikemura et al.,[3] the aromatic compounds were not identified in their experiments. This may be because of differences in reaction temperature and pressure. Eighteen to 20 peaks were identified by VPC as Benzene, toluene, xylene, n-pentane, n-hexane, n-heptane, n-octane, cyclohexane, and methylcyclohexane, and, in special cases, as heptene-1 and hexene-1.

Thermolysis without steam pressure was carried out under similar conditions to investigate the role of water. Heating was effected under slight nitrogen pressure to avoid oxidation. Experimental conditions and results are listed in Table III. The following conclusions were derived from the comparison of Table I with Table III.

(1) Gasification and coke deposition proceed more quickly in thermolysis without steam pressure. Accordingly, the production of the liquid fraction was more effective under steam pressure. The composition of the gaseous product did not differ.

(2) The yield of LBP was slightly different.

(3) A remarkable difference of the fraction determined by FIA was not observed at 425°C. In thermolysis without steam at 450°C, the saturated hydrocarbons decreased with reaction time. This is apparently due to a combination of dehydrogenation and decomposition reactions. However, there were fewer olefins formed with steam, while there were more aromatics formed than in steam. In thermolysis under steam pressure at 450°C, the saturated hydrocarbons increased, reached a maximum, and then decreased with reaction time. Although the yield of aromatics is not as large as those without steam, a sizable amount was observed.

(4) Decomposition of PE was depressed by steam pressure. However, contrary to expectations by pressure difference, no noticeable inequality was found.

The most appropriate temperature for the production of the low molecular aromatic compound is 450°C. The following three routes can produce aromatic hydrocarbons:

(1) Diels–Alder type bimolecular reaction.

(2) Dehydrogenation from paraffins via naphthenes as

$$n\text{-}C_6H_{14} \longrightarrow \bighexagon + H_2 \longrightarrow \bighexagon + 3H_2$$
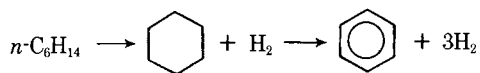
(3) Unimolecular ring formation of paraffins accompanied by dehydrogenation via olefins as

$$n\text{-}C_6H_4 \longrightarrow n\text{-hexene} \longrightarrow \bigbenzene + 3H_2$$
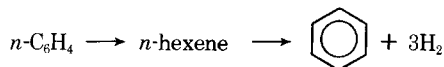
Application of high pressure is theoretically advantageous to route (1). However, this tendency was not found in experimental results. Moreover, the monomer concentration obtained by thermolysis of PE was reported as 0.03% at 500°C,[4] and our reaction was studied in dilution with steam. Therefore, the main route of this thermolysis is not (1) but (2) or (3). If (2) were the main route, the yield of methylcyclohexane should decrease with increase in toluene; however, the experimental result showed a constant or a slightly reverse tendency. Moreover, the peaks of hexene-1 and heptene-1 observed in the initial stage,

TABLE III
Experimental Conditions and Results in Thermolysis Without Steam Pressure

| Reaction condition | | Product | | | Analysis of LBP | | | | | |
Temp., °C	Time, hr	Gaseous, bar	Liquid, wt % Total	Liquid, wt % LBP	FIA, vol % Aromatics	FIA, vol % Olefins	FIA, vol % Saturated hydrocarbons	VPC, wt % Benzene	VPC, wt % Methyl cyclohexane	VPC, wt % Toluene
425	2	5.6	46.7	26.5	24.0	34.2	41.8			
	4	7.0	36.4	21.9	27.0	19.4	53.6			
450	0	5.0	47.1	28.4	19.0	30.7	50.3	3.89	2.03	4.09
	2	9.5	24.2	15.1	46.8	8.5	44.7	5.24	2.20	8.33
	4	12.7	19.8	10.6	55.0	6.9	38.1	7.44	1.89	12.66

which were not determined quantitatively because they were in trace amounts, disappeared with reaction time. Hence, the main route to produce aromatic hydrocarbons is (3).

Thus, we assume the route from PE to aromatics as follows:
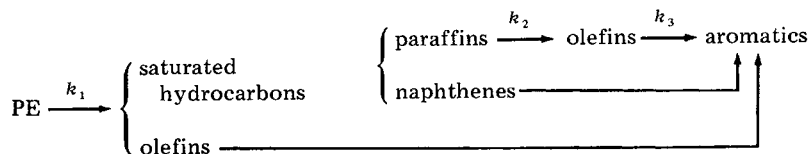
It has been reported that[5] both reaction rates are nearly the same ($k_2 = k_3$) in successive reactions such as paraffins → olefins → aromatics. The yield of paraffins (saturated hydrocarbons) should decrease with increase in aromatics. There are no paradoxes in the case of thermolysis without steam. However, unlike the thermolysis without steam, the content of saturated hydrocarbons increased experimentally up to a certain value in thermolysis under steam pressure. The explanations for this phenomena are as follows.

Assuming that saturated hydrocarbons (paraffins) are intermediate products of the successive reaction from PE to olefins when there are differences in the ratio of the reaction rate constant between the thermolysis with and without steam [$(k_1/k_2)_{steam}$ and (k_1/k_2)] under conditions of $k_1 \gg k_2$, the time reached to the maximum yield of the intermediate,

$$t_{max} = \ln \frac{k_2/k_1}{k_2 - k_1}$$

should be different. Saturated hydrocarbons after t_{max} without steam and mainly before t_{max} with steam were obtained. The value of t_{max} under steam pressure is nearly equal to 3 hr. Tentatively, the value of t_{max} without steam is equal to zero as far as the expression of Table III is concerned. The ratio can be estimated as $(k_1/k_2)/(k_1/k_2)_{steam} = 10$–$20$.

This is because the difference in reaction pressure, that is, the reaction pressure of the thermolysis with steam, is about 180–200 bar, and this large steam pressure depresses the decomposition of PE as compared with the thermolysis in the absence of steam. Unfortunately, we cannot conclude at present on the individual pressure effect of k_1 and k_2. A definite theory on the thermal decomposition of hydrocarbons has not been presented yet. Only a qualitative relationship indicates that hydrocarbon formation accelerates up to a certain pressure and decreases at excess pressure.[6] It is probable from the above scheme that k_2 accompanied by the generation of hydrogen is more depressed than k_1 with pressure.

Hydrogenolysis

Although the thermolysis under steam pressure can reach sufficient liquefaction at the appropriate reaction temperature, a considerable amount of unsaturated hydrocarbons is included in the reaction product. Hydrogenolysis is necessary to refine the product.

In hydrogenolysis of organic polymers a catalyst is used. Since the final object of this study is the development of a process for recovering hydrocarbons from industrial waste, an expensive catalyst is not practical even if it has a strong activity. We studied mainly the hydrogenolysis without a catalyst. Some ex-

TABLE IV

Experimental Conditions and Results of Hydrogenolysis Under Steam Pressure

Reaction condition				Gaseous, bar	Product			Analysis of LBP					
					Liquid, wt %		Solid, wt %	FIA, vol %			VPC, wt %		
Temp., °C	Pressure, bar	Time, hr	H$_2$,[a] bar		Total	LBP		Aromatics	Olefins	Saturated hydrocarbons	Benzene	Methyl cyclohexane	Toluene
425	190	0	10	11	—	—	Greasy						
		2		11	64.1	36.3	0.0	12.4	28.8	58.8			
		4		11	42.3	27.1	0.0	16.3	19.8	63.9			
450	205	0	10	11	63.1	32.6	0.0	12.5	37.2	50.3	2.39	2.34	3.32
		2		12	32.7	16.7	0.0	27.5	18.2	54.3	2.85	4.88	7.46
		3		13	33.2	22.6	0.0	28.7	11.9	59.4	3.44	4.22	7.97
		4		13	32.2	20.0	0.0	31.6	10.4	58.0	4.21	4.99	10.03
450	270	0	40	36	62.0	47.9	0.0	3.8	14.0	82.3			
		2		35	42.1	34.5	0.0	4.8	4.0	91.2			
		3		33	34.2	26.3	0.0	7.4	3.7	88.9			
450	340	0	70	63	43.8	34.6	5.0	2.7	2.9	94.4			
		2		62	18.6	15.5	→	2.5	2.0	95.5			
		3		60	16.3	12.5	decrease	2.8	trace	97.2			
450	410	0	100	93	43.8	32.6	6.0	2.8	3.0	94.2	1.14	3.59	0.00
		2		90	21.9	18.2	→	2.8	2.0	95.2	3.17	6.00	0.00
		3		86	14.8	12.1	decrease	2.6	2.0	95.5	3.63	7.24	0.00

[a] Initial pressure.

TABLE V

Molar Ratio of C_2–C_4 Gaseous Products to Methane in Hydrogenolysis Under Steam Pressure

| Reaction condition | | | | | | | |
H_2,[a] bar	Time, hr	C_2H_6	C_3H_8	n-C_4H_{10}	i-C_4H_{10}	Butene-1	Butene-2
10	0	1.14	1.19	0.37	0.03	0.11	0.05
	2	0.75	0.61	0.21	0.04	0.03	0.02
	3	0.65	0.49	0.14	0.04	0.01	0.01
	4	0.68	0.56	0.18	0.05	0.01	0.02
40	0	1.36	1.36	0.39	0.06		
	2	1.13	1.01	0.23	0.05		
	3	1.07	1.01	0.24	0.07		
70	0	1.76	1.79	0.99	0.25		
	2	1.65	1.47	0.33	0.08		
	3	1.31	1.28	0.25	0.06		
100	0	2.91	5.94	2.55	0.29		
	2	1.73	1.96	0.54	0.09		
	3	2.28	3.88	1.34	0.23		

[a] Initial pressure.

periments using ferric oxide (Fe_2O_3) as a catalyst were conducted for comparison. It should be emphasized, however, that the catalytic effect of the reactor wall and steel balls that are used for sufficient mixing in the reactor is not negligible. The added catalyst in this study is Fe_2O_3. The reaction temperature of the hydrogenolysis is 450°C.

Experimental conditions and results in the hydrogenolysis are shown in Tables IV and V. The composition of the gaseous products with initial hydrogen pressure of 10 bar was the same as with thermolysis. However, butene-1 and butene-2 disappeared over 40 bar initial hydrogen pressure. The exhaustive hydrogenation of the gaseous product requires a supply over 40 bar initial hydrogen pressure in our apparatus. The gaseous olefins were obtained by a lack of the reactant hydrogen at 10 bar. A molar ratio of each gaseous product to methane increased with increasing pressure, suggesting that the degradation to low molecular weight compound is difficult to achieve under pressure.

The liquid products were low in viscosity, dark-brown in color at initial hydrogen pressure 10 bar, and yellowish above this pressure. The saturated hydrocarbons increased with initial hydrogen pressure and were constant at about 95 vol % at 70 and 100 bar hydrogen pressures. These phenomena caused the oversaturation of the hydrogen feed at these pressures. Accordingly, the olefins decreased and were constant at 70 and 100 bar. The aromatics showed a similar tendency and supported the reaction schemes mentioned in the preceding section. The reaction temperature at 450°C is appropriate for the production of the aromatics in thermolysis. However, the dehydrogenation of olefins or naphthenes are less effective in the presence of sufficient hydrogen pressure. Therefore, the reaction condition with insufficient hydrogen feed as initial hydrogen pressure of 10 bar is an intermediate state between thermolysis and hydrogenolysis. The composition of the liquid product demonstrated intermediate behavior. The yield of the liquid product increased with initial hydrogen pressure, reached a maximum at 40 bar, and decreased above this pressure.

Effects of steam pressure and catalyst are shown in Tables VI and VII. Liquefaction is accelerated and gasification is suppressed with increasing steam

TABLE VI
Effects of Stream Pressure and Catalyst on Hydrogenolysis at 450°C[a]

Reaction condition				Product				FIA of LBP, vol %		
					Liquid, wt %					
H$_2$O, g	Fe$_2$O$_3$, g	H$_2$,[b] bar	Pressure, bar	Gaseous, bar	Total	LBP	Solid, wt %	Aromatics	Olefins	Saturated hydrocarbons
60		70	342	63	43.8	34.6	5.0	2.7	2.9	94.3
30		70	248	67	43.0	33.8	4.7	3.2	4.8	92.0
15		70	207	63	53.1	41.8	0.5	2.4	3.0	94.6
60		40	272	36	62.0	47.9	0.0	3.8	14.0	82.3
30		40	192	37	61.1	40.0	0.0	5.0	19.0	76.0
15		40	151	38	54.6	37.9	0.0	5.1	14.4	80.5
60	3.0	70	328	65	53.4	28.6	5.6	2.9	7.5	89.6
30	3.0	70	220	65			4.6			

[a] Reaction time, 0 hr; PE, 30 g.
[b] Initial pressure.

TABLE VII
Effect of Steam Pressure on Molar Ratio of C_2–C_4 Gaseous Products to Methane in
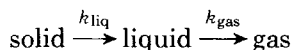Hydrogenolysis at 450°C[a]

Reaction condition					
H_2,[b] bar	H_2O, g	C_2H_6	C_3H_8	n-C_4H_{10}	i-C_4H_{10}
40	60	1.77	1.79	0.99	0.25
	30	1.85	2.39	0.82	0.13
	15	1.75	2.10	0.61	0.12
70	60	1.37	1.37	0.39	0.06
	30	1.44	1.64	0.39	0.06
	15	1.28	1.28	0.28	0.04

[a] Reaction time, 0 hr.
[b] Initial pressure.

pressure.   The excess decomposition was retarded at higher pressures because the water feed is proportional to the reaction pressure.   Ferric oxide showed a sufficient catalytic activity under steam pressure: the liquid products increased in the presence of 10 wt % Fe_2O_3 (the olefin content is somewhat larger); however, the yields of the solid product were independent of the catalyst.

There are characteristic differences between thermolysis and hydrogenolysis. A considerable amount of solid residue was recognized and the gasification proceeded (low yield of the liquid product) above 70 bar as the initial hydrogen pressure.   This observation shows that k_{liq} decreases and k_{gas} increases in the model for successive reactions from

$$\text{solid} \xrightarrow{k_{liq}} \text{liquid} \xrightarrow{k_{gas}} \text{gas}$$

The hydrogenolysis of PE proceeds according to the following steps: (1) Generation of radicals by the random scission of polymer chain.   This is accompanied by the intermolecular hydrogen abstraction by the generated radical from the other radicals.   (2) Radical transfer to the catalytic surface.   (3) Hydrogenation at the surface.   Overall rate equation can be expressed as $w = k[R\cdot][H_2]$.   (4) Desorption of the hydrogenated product from the surface.   Step (1) is the same reaction with the thermolysis; this process is somewhat depressed with pressure.   It is probable that steps (2) and (4) are considerably depressed with pressure.   Step (3) is remarkably accelerated with hydrogen pressure.

At higher hydrogen pressure, the hydrogenation of small radicals increases more with large radicals because of the difference in diffusion velocity in relation to the catalytic surface.   Gasification, therefore, is accelerated in spite of the presence of solid residue.   The reaction profile shows a low yield of liquid product having intermediate molecular weight.   Experimental runs at 70 and 100 bar as initial hydrogen pressure agree with these data.

On the other hand, at lower hydrogen pressure, the radical generated from the decomposition of PE transfers smoothly to the catalytic surface.   However, the hydrogenation reaction is comparatively slow.   Therefore, although liquefaction proceeds sufficiently, a considerable amount of unsaturated compound resides in the hydrogenation products.

In this process, thermolysis and hydrogenolysis can simultaneously proceed in principle; therefore, if we can select suitable reaction conditions, both reactions

can be balanced and low gasification and high liquefaction can be reached. This suitable reaction condition corresponds to 40 bar initial hydrogen pressure (1 mole hydrogen to 1 mole monomeric unit of PE). The yield of the liquid product reaches a maximum and includes over 80 vol % saturated hydrocarbons at this pressure. Such a reaction condition is desirable to a decrease in unsaturated compounds.

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