

WASTE PLASTIC GASIFICATION AND HYDROGEN PRODUCTION IN SUPERCRITICAL WATER

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We developed a new technique to produce hydrogen gas from waste plastics in supercritical water. We investigated the effects of the reaction temperature, pressure, time, kind of catalyst and mole ratio of water to plastics on the plastic decomposition rate and the hydrogen production yield. From the experimental results, high temperature around 700°C and high molar ratio of water to plastics were favorable for the hydrogen production, while the reaction pressure was case by case. Low pressure was better for easily-decomposing-plastics such as polyolefin, and high pressure was more effective for others. Two kinds of catalysts were examined: nickel and alkaline. Comparing these catalysts, alkali catalyst gave more excellent performance in the repetition of the catalyst and the cost.

INTRODUCTION

Recently the recycling of wastes is expected strongly from the viewpoint of the environmental defense and the effective use of the resources. Among many kinds of wastes, waste thin electric cable and the shredder dust, which is discharged from the final process of disposal of the waste automobile and waste electric appliances, are difficult to treat. The waste electric cable contains polyvinyl chloride and copper. On the other hand the shredder dust contains many kinds of materials such as halogenated plastics, thermosetting resins, thermoplastic resins, metals, glasses and others. Today's disposal is only landfill in Japan.

Supercritical water ($T_c=374^\circ\text{C}$, $P_c=22.1\text{MPa}$) is a promising solvent for the decomposition of organic waste materials. It is used to liquefy waste plastics to oil[1], hydrolyze waste biomass to monomers[2] and dehalogenation of waste GFRP[3]. Recently the hydrogen production from biomass and organic waste has attracted much attention and several researches are reported[4-6]. However, this technique has several problems to break through. One of the difficult problems is a catalyst. It is important to find a proper catalyst working in supercritical water, which is active, cheap, used from repetition to repetition.

In this work, we investigated the gasification of dechlorinated polyvinyl chloride, which is called polyene, and polyethylene using supercritical water. The effects of the reaction temperature, pressure, time, kind of catalyst and mole ratio of water to plastics on the plastic decomposition rate and hydrogen production yield were studied using a batch reactor.

I - MATERIALS AND METHODS

Table 1 shows the element analysis and structural formula of samples. In this experiment, polyethylene and polyene were used for the gasification with supercritical water. Polyene was provided as follows: polyvinyl chloride was dechlorinated at 380 °C and 30 min in nitrogen gas ventilation. Nickel (Ni-5132P provided by N.E.Chemcat Co.), KOH or NaOH was used for the gasification catalyst.

Figure 1 shows the experimental apparatus used for the gasification. This apparatus had a

batch reactor made of SUS316 and having about 9ml in inner volume with 1/2 inches in o.d. and 150mm long. The experimental procedure is as follows. The plastic, distilled water and catalyst were loaded into the reactor. Then the air in the reactor was replaced with nitrogen gas. The reactor was closed and heated to a reaction temperature in an electric furnace. It took about 15min for the reactor to increase from the room temperature to the setting reaction temperature around 700°C. After reaching the reaction temperature, small amount of distilled water was added into the reactor using a high pressure pump in order to adjust the reaction pressure. After a given reaction time, the furnace was turned off and opened, and the reactor was cooled quickly with the electric fan.

The gaseous product was collected into a sampling bag and analyzed using gas chromatographs (Shimadzu GC-8A with Molecular Sieve 5A for the analysis of hydrogen, and GC-14B with Porapak Q for the analysis of hydrocarbons and CO₂) equipped with thermal conductivity detectors. The gaseous product was put out from a sampling bag with a gas syringe and its volume was measured. Next, the liquid and solid products in the reactor were collected with distilled water and filtered. The filtrate was analyzed by TOC (Shimadzu TOC-VCSN) to determine the organic carbon dissolving in water. The solid was stirred in HCl aqueous solution about 3 hours. The catalyst was dissolved in the solution and the remaining solid was the residue. After the filtration and washing, the residue was dried at 60 °C in the oven about 12 hours and weighed in order to determine the decomposition ratio of plastics.

Table1 Element analysis and structural formula of samples

	Element analysis [wt%]			Structural formula
	C	H	Cl	
Polyethylene	85.7	14.3	-	$-(\text{CH}_2 - \text{CH}_2)_n-$
Polyene	91.7	7.6	0.68	$-(\text{CH} = \text{CH})_n-$

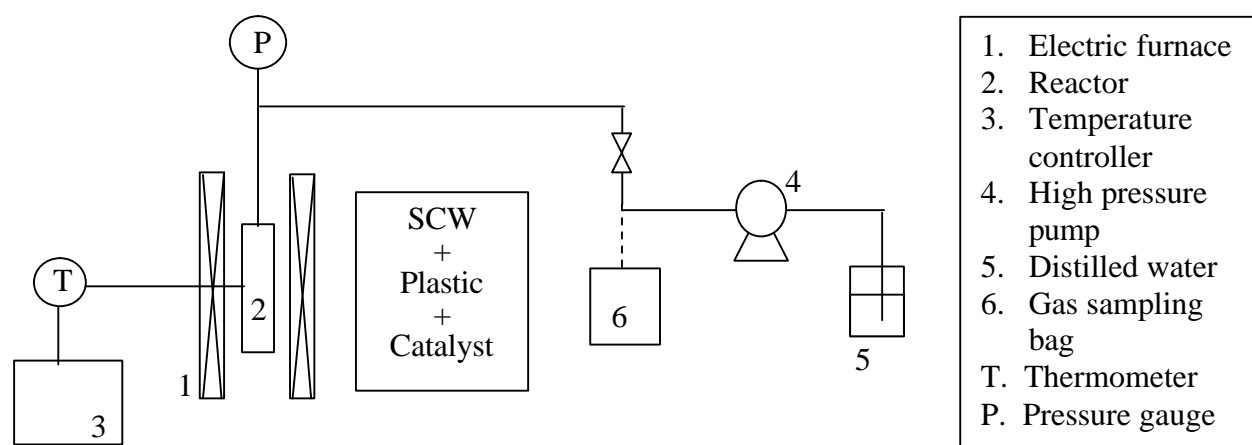


Figure 1 Experimental apparatus for SCW gasification

? -RESULTS AND DISCUSSION

Figure 2 shows the effect of the catalysts on the amount of gaseous product at 700°C, 30MPa, 30min and mole ratio of water to carbon of sample of 20. The amount of the catalyst was 20wt% for the sample. The y-axis represents the volume of the gaseous product at 25°C and 101.3kPa for 1g of the sample. Using the nickel catalyst, polyethylene was decomposed completely and 1650ml of hydrogen gas was produced, which corresponded to 53% of the total gaseous product. When it was gasified using KOH or NaOH catalyst, 1340ml or 1220ml of hydrogen gas was obtained, respectively. On the other hand, 1500ml, 1340ml or 1100ml of hydrogen gas was produced from polyene with nickel, KOH or NaOH catalyst. About 70% of polyene was decomposed using all kinds of catalysts. The results were indicated that the order of the catalytic activities for hydrogen production was nickel > KOH > NaOH and that of the total volume of the gas produced was also nickel > KOH > NaOH.

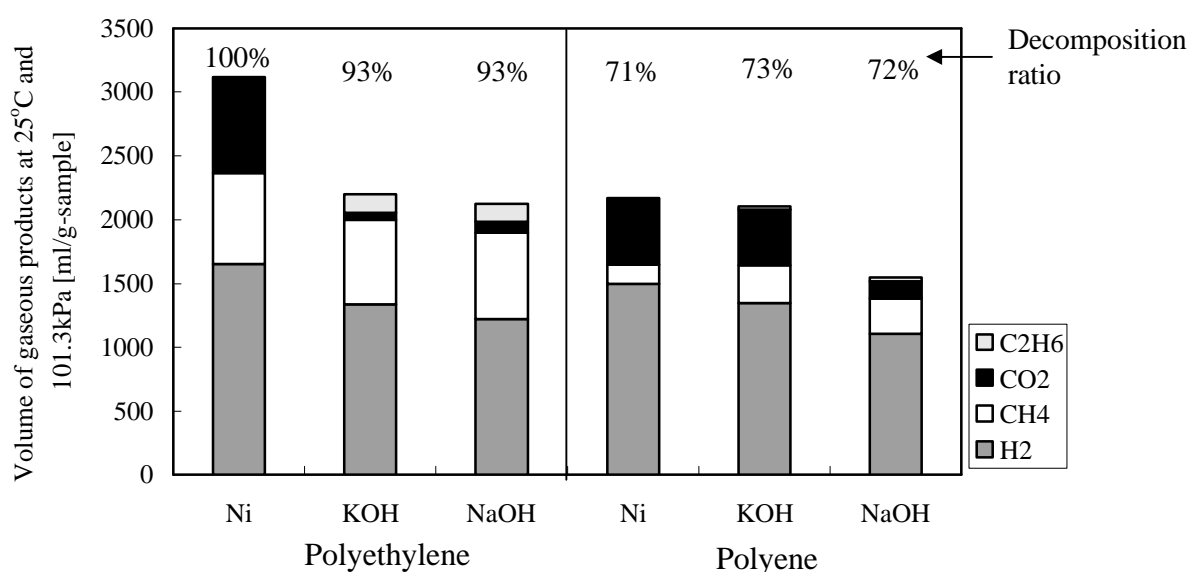
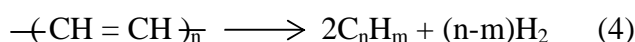
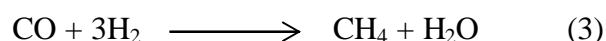
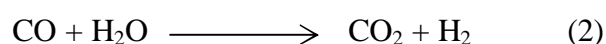
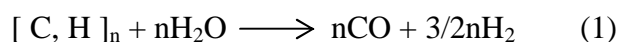


Figure 2 Effect of catalysts on hydrogen production for SCW gasification (700 °C, 30MPa, 30min, H₂O/C=20, 20wt% of catalyst)

The main reactions of the gasification of the plastics consisting of only hydrogen and carbon atoms with supercritical water are given as follows :



The decomposition ratio of polyene was smaller than that of polyethylene. However the reaction (4) accelerated the hydrogen production from the polyene residue. As a result, the amount of hydrogen production for polyene was almost the same as that for polyethylene.

Figure 3 shows the origin of hydrogen gas for the gasification of polyethylene and polyene using KOH catalyst. The y-axis is the volume of hydrogen from 1g of sample. The bar graph

on the left hand side for each plastic (Gaseous products) shows the virtual volume of hydrogen gas from hydrogen, methane and ethane, when all hydrogen atom in the product would be hydrogen gas. The bar graph on the right hand side (Origin of hydrogen) shows the produced volume of the hydrogen gas from each origin. The major origin of hydrogen was the plastics. The hydrogen gas was released from the plastics after the decomposition. For example, 56% and 47% of hydrogen gas was produced from polyethylene and polyene, respectively. However other origin of hydrogen was required: 44% for polyethylene and 53% for polyene. Judging from the successive chemical reactions in (1)–(4), the second origin might be water. In this case, active supercritical water reacted with carbon monoxide to produce hydrogen gas.

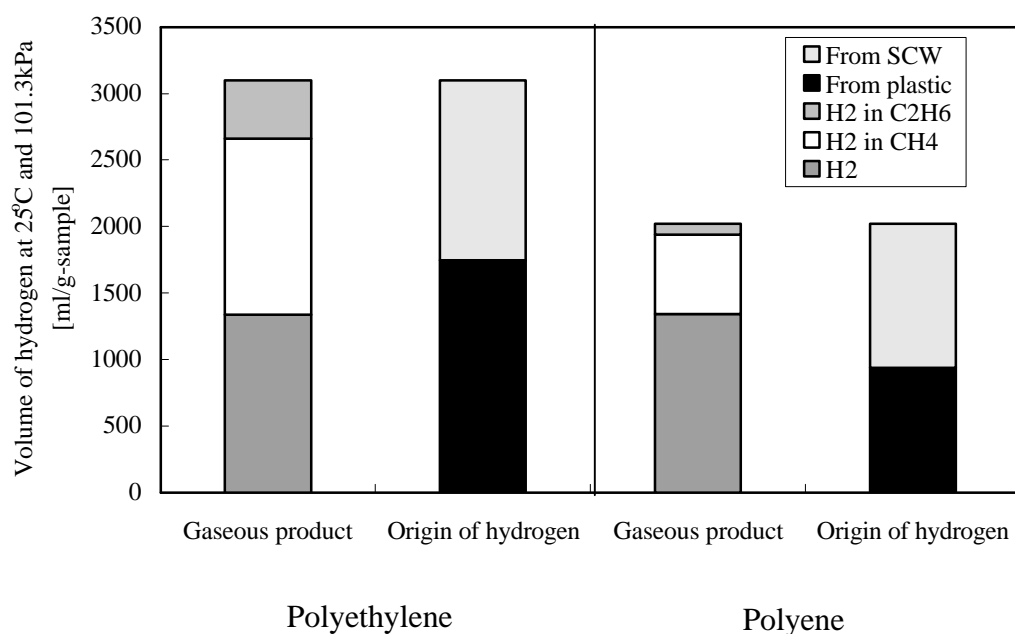


Figure 3 Origin of hydrogen gas in gasification of plastics (700°C, 30MPa, 30min, H₂O/C=20, 20wt% of KOH)

Figure 4 shows the pressure dependence of the volume of gaseous product at 700°C, 30min and 100wt% of KOH catalyst. In the case of polyethylene, the decomposition ratio hardly changed with pressure, but the volume of hydrogen gas decreased from 4700ml at 10MPa to 3600ml at 30MPa for 1g of sample. In the case of polyene, the decomposition ratio increased from 68% to 77%, when the pressure increased from 10 to 30MPa. The amount of hydrogen gas increased from 1500ml to 2060ml for 1g of sample, when the pressure increased. The pressure effect between two plastics was opposite each other. For polyethylene, the progress of reaction (1) at 30MPa was almost the same as that at 10MPa. The reaction (2) was not affected by pressure because there was no change in the total number of moles before and after reaction. However, the reaction (3) was accelerated to the product side and the hydrogen was consumed, when the pressure increased. As a result, the hydrogen production decreased when the pressure increased. On the other hand, for polyene, the progress of reaction (1) at 30MPa was higher than that at 10MPa. The reaction (1) was promoted to the product side and the hydrogen gas and carbon monoxide, which was used to produce hydrogen, were produced much. As a result, the amount of hydrogen increased when the pressure increased.

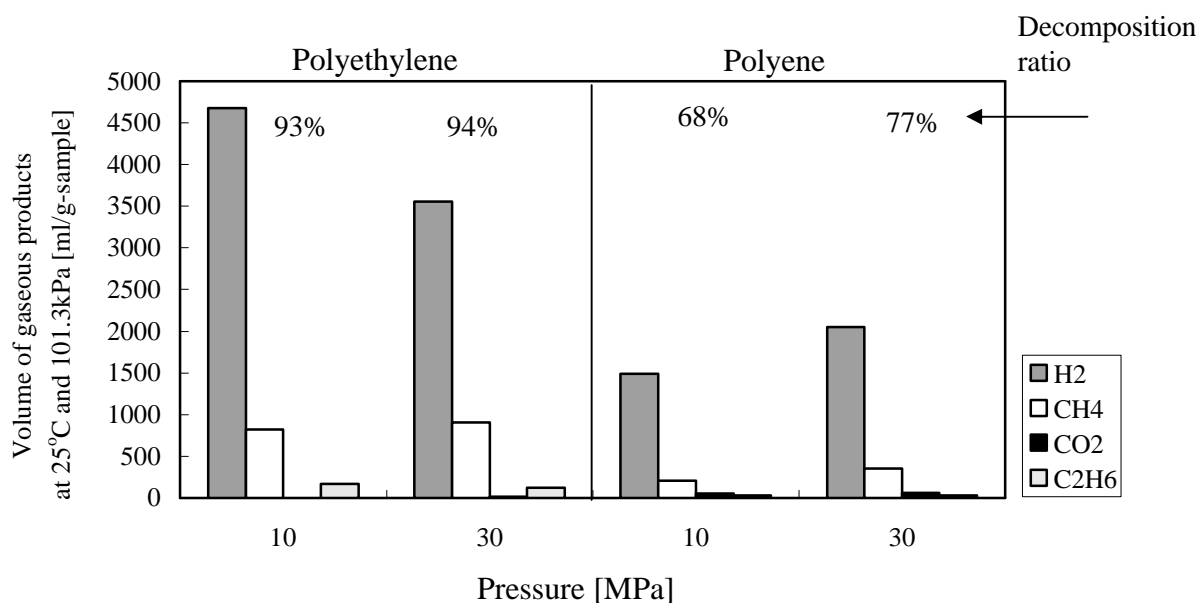


Figure 4 Pressure dependence of volume of gaseous products in supercritical water gasification of plastics (700°C, 30min, H₂O/C=20, 100wt% of KOH)

The repetition of the catalyst was examined. The nickel catalyst was difficult to regenerate the activity. On the other hand, alkali catalyst was recovered as the corresponding carbonate compound covered with a polymeric material. In the gasification, as the carbonate catalyst had almost the same or a little bit smaller activity than alkali catalyst, the repetition of the alkali catalyst was possible after a coating polymeric material was burned completely. The result is shown in Figure 5. KOH catalyst after heating treatment, which converted to the corresponding carbonate, gave the same performance for the hydrogen production. We can use this type of catalyst many times.

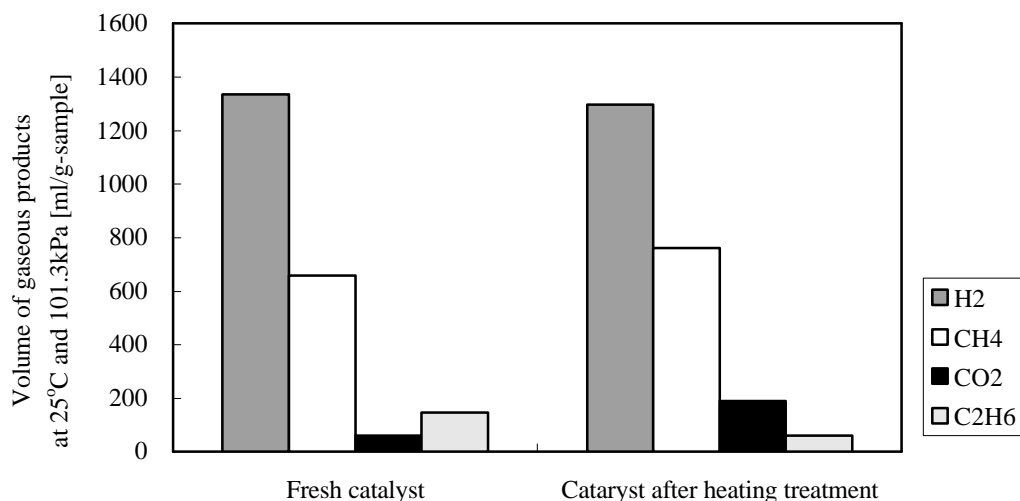


Figure 5 The repetition of KOH catalyst (700°C, 30MPa, 30min, H₂O/C=20, 20wt% of KOH)

CONCLUSION

We investigated the supercritical water gasification of polyethylene and polyene with nickel, KOH or NaOH catalyst. At 700°C, 30MPa, the order of catalytic activity for hydrogen production was nickel > KOH > NaOH. The hydrogen was supplied from both plastic and water. Around half of hydrogen was produced from water by the water gas and water-gas-shift reactions. The alkali catalyst could be used repeatedly without the decrease in the catalytic activity.

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