[Review Paper]
Recycling Possibilities of Organic Waste by Hydrothermal Process

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Hydrothermal solution is wide open to have a wide possibility for reaction media from the range of ionic to radical reactions. The hydrothermal solution around at critical point have a wide variation of dielectric constant from 80 to 2 depend on P-T conditions. The choice of suitable reaction media therefore, can be easily controlled by selecting just the P-T conditions.

Further, the ion product (Kw value) shows a maximum value around at 250°C, and as a result, the water at this temperature range have a maximum hydrolytic ability and perform a perfect decomposition of toxic and hazardous materials, such as dioxin, PCBs, freons, etc. Using steam having a pressure below saturated vapor pressure at high temperature range, organic polymer is easily decomposed to monomer and the coal to liquefy and gasify. In this paper, the author aimed to evaluate the employment of the mini-autoclave and the practicality of continuous tube reactor and its application for decomposition of halogenated organic compounds, degradation of coal, liquefaction of polymer and rubber, as described.

1. Characteristics of Hydrothermal Solution Containing Supercritical Water

Water has a specific characteristic among various solvents. Further, the hydrothermal solution at above 100°C show unique properties compared to those at ambient solutions shown in Fig. 1, a variation of physical properties as a function of the temperature of water1) at above 100°C in traditional autoclave. The saturated vapor pressure (P) increases with temperature, while other parameter such as surface energy (γ), dielectric constant (ε), density (ρ), and viscosity decrease with rise in temperature. Another characteristic of hydrothermal reaction is in the high reaction velocity in the solution, and as a result the continuous flow system autoclave2) using the tube digester has been found to have potentials for wide application for censers and computer control. Using the continuous tube type autoclave, the P-T conditions can be independently controlled by an external pressure pump system as compared to ordinary batch type autoclave using only unsaturated. The characteristic of hydrothermal reaction is usually its great hydrolysis function. Hydrolysis is generally presented on acidic and alkaline catalytic reaction corresponding to objective materials, while the magnitude of hydrolysis capacity can be explained by the Kw value, which is largely affected by temperature. Shown in Fig. 2 are Kw values at various temperature3).

On the other hand, the selectivity of reaction media is affected by the dielectric constant. Large values of about 80 are suitable media to enhance an ionic reaction such as complex decomposition of ionic compounds, although the Kw values under 10 are good media as organic reactions. These dielectric constants (ε) are largely affected by density.

E. U. Franck4) has reported iso-ε curves with isobar curves as a relation of temperature and density as shown in Fig. 3. The dielectric constant increases with pressure at the range of high density region and at contrast decreases with pressure at high temperature region. The P-T relation of water and a typical reaction example at each suitable reaction media, as well as, the variations of saturated vapor pressure curves of

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organic and inorganic solute solutions at the $P$-$T$ region are shown in Fig. 4. The non-polar organic compounds contained polymer and resin, which easily dissolve in water with low dielectric constant under high temperature (above $T_c$) and low pressure, and so these low dielectric fields are suitable reaction media to enhance organic reactions. In the region of high temperature above 500°C pyrolysis of organic substance is easily promoted from a pitch and/or char by radical condensation. Arai and Adschiri had studied the selective decomposition to form glucose using a very high velocity reaction.

2. Possibility of Waste Treatment by Using of Hydrothermal Reaction Media

The wastes generally are mixture of various components. Thus it becomes necessary to selectively separate each component. Subcritical hydrothermal reaction of solid powders, using an ordinary batch autoclave, is a typical heterogeneous reaction of gas-liquid-solid phase, and accordingly the estimation of reaction process is generally difficult. Since an injection pump and pressure controlled valves are attached to the tube reactor, the suitable conditions of $P$-$T$ can be easily selected. Hence under these conditions the constituents of waste materials might be separated by the $P$-$T$ control using the continuous variation of hydrothermal characteristics. In addition, the application of this process is expected for the application of the supercritical chromatography containing subcritical region. Thus, any type of compounds containing inorganic and organic materials may be separated using this novel apparatus. Moreover, the resin and polymer waste are commonly difficult to separate among each component. Polymers and resins including halogen, nitrogen, sulfur, phosphorus, etc. in incineration furnace decompose to generate acidic products. Accordingly this acidic products cause not only the corrosion of furnace, but also promote environmental contamination.

It is well known that coal, heavy oil, polymers of rubber and plastics, and resins used in printing of semiconductor can easily be liquefied and gasified at lower pressure side, at above critical temperature. Using alkaline alcoholic solution at temperature around 300°C, the hetero-compounds containing halogen, nitrogen, sulfur and phosphorus easily decomposed without corrosions, by the reason of acceleration of hydrolysis with high $K_w$ values and reductive and dispersing of hetero-compound by alcohol.

3. Application of Mini-autoclaves to Collection of Basic Data

As a means to examine the possibility of recycling of waste materials by the hydrothermal process, the simple and small batch autoclaves are effective and useful.
A large scale autoclave with various equipment has several disadvantages, such as heterogeneous temperature distribution, low safety, troublesome control and inefficiency. The mini-type autoclave, such as Morey’s cylinder vessel, however is effective in safety, handling and fitting to experiment requirements. The improved mini-autoclave and its application to the treatment of waste materials are introduced in this paper.

Shown in Fig. 5 are some mini-autoclaves. The mini-autoclave (a) type made of case hardened steel with soft metal gasket (copper) which prevent leakage of the hydrothermal solution above 300°C. The (b) type vessel has inside chamber made of hastelloy, inconel, titanium alloy, and Pt to withstand corrosion under acidic and oxidative conditions. The (c) type autoclave is equipped with a pressure valve which is used in the case of using high pressure gas and collecting generated gas. These autoclaves are easily handmade. The rapid heating system with stirring apparatus is shown in Fig. 6. As a means to improve homogeneous and rapid heating, a vessel made of magnetic material encompassing an induction heating furnace was employed. This system makes possible to attain a rapid temperature rise exceeding 100°C/min. Further, stirring method is an important factor in hydrothermal process and the type of stirring system affects the reaction. The rotating propeller blade system in static vessel only allows to rotate the species to react without mixing of heterogeneous phases. The most effective stirring system that was recently developed consist of perpendicular shaking movement. The shaking furnace combining with high speed heating and rocking movement is shown in Fig. 6. Using these equipment, the experimental data of pressured gas-hydrothermal conditions can be collected, with a good reproduction.

4. Some Examples of Organic Waste Treatment

4.1. Decomposition of Halogenated Organic Waste under Subcritical Conditions

The hydrothermal solution at around 300°C exhibits a maximum $K_w$ value in conditions of saturated vapor pressure and it is expected as the most powerful hydrolysis media for degradation of hetero-bonding organic compounds. As a means to obtain the same $K_w$ values in supercritical water as that in subcritical temperature range of 250-300°C in same density, an extremely high pressure is needed, as shown in Fig. 3.

That is, the strong electrophilic and/or nucleophilic elements and groups, compared to carbon atom, exhibit electron preference among chemical bond of respective element/group and carbon.

These chemical bonds are easily hydrolyzed by acidic and alkaline catalyst, corresponding to alkaline and acidic products.

4.1.1. Hydrothermal Decomposition of Chlorofluoro Carbons

Shown in Fig. 7 are the results of hydrothermal decomposition of CCl₃F. Various halogenated organic compounds are insoluble in water whereby the first step of reaction may occur at the intersurface. The additions of alcohol show dramatic effects. They lower the decomposition temperature for about 100°C. Shown in this figure is the initial stage of the decomposition occurring in tests conducted at several temperatures and environmental conditions.
4.1.2. Hydrothermal Decomposition of Other Chlorinated Organic Compounds

The chloroalkanes, chloromethane and chloroethane, trichloroethylene, and so on, easily decompose in the same conditions as in the case of CCl3F. The decomposition of stable aromatic compounds such as PCBs, Dioxines, chlorobenzenes requires higher temperature approximately 350°C and the use of same solvent8)-10).

The reaction products are halogenide ion in water phase and among other organic products such as alcohols, phenols and their derivatives. Wastes containing these halogenated organic materials are commonly the environmental contaminants, attributed to its stability and toxicity. The toxicity is based on halogen, and as a result the perfect release of halogen from organic molecule to ion in water could be expected. A successfully decomposed chloride ion is easily dissolved in alkaline water solution and, therefore a perfect decomposition may be expected.

On the other hand, hydrogen chloride and/or chlorine molecule were easily formed as decomposition products in supercritical and pyrolytic conditions. The reaction products are halogenide ion in water phase and among other organic products such as alcohols, phenols and their derivatives. Wastes containing these halogenated organic materials are commonly the environmental contaminants, attributed to its stability and toxicity. The toxicity is based on halogen, and as a result the perfect release of halogen from organic molecule to ion in water could be expected. A successfully decomposed chloride ion is easily dissolved in alkaline water solution and, therefore a perfect decomposition may be expected.

The main products are alcohol and its derivatives from alkane groups, and phenol and its derivatives from aromatic groups. Byproducts from alkanes are olefins and from aromatics are biphenyl compounds, and, therefore, release of hydrogen chloride molecule may occur both inter and intra molecules. When trichloroethane was used, n-hexane was formed by hydrolysis with only pure water. It is expected that n-hexane may be formed by hydration substitution of chlorine and condensation.

The reaction mechanism of decomposition of halogenated organic compounds under hydrothermal conditions cannot be explained using the simple model of SN2 in ambient conditions. Moreover, the chlorinated organic compound contain same numbers of chlorine and hydrogen in molecule decomposed with hydrogen chloride to form amorphous carbon, and in some cases graphite11).

4.2. Liquefaction and Gasification

4.2.1. Degradation of Oxygenated Organic Compounds in Sub-critical Conditions

Other types of oxygenated organic materials, originated from plants such as starch, cellulose, lignin etc., are easily decomposed with decarbonation to form alkanes under sub-critical alkaline hydrothermal conditions. Low grade coal as lignite containing large amounts of oxygen could be easily liquefied12) under alkaline hydrothermal conditions, as shown in Fig. 8 to form alkanes, CO2 and H2 gas as shown in Table 1. It is generally explained that the petroleum may be formed by oceanic animal bacteria by the reason of its aliphatic hydrocarbons contained. However, other
possibilities can be brought to mind. Aliphatic hydrocarbons are easily formed by alkaline decarbonation from carbon hydrates contained in plants. In addition, the decarbonation is accelerated by Ca$^{2+}$ and Mg$^{2+}$ in sea-water to form the carbonate. The ceiling rocks of petroleum reservoir consist of carbonate minerals. Besides, the liquefaction of oxygenated organic compounds may be applied to the treatment of non-used biomaterials such as sewage sludge and waste from paper industries.

4.2.2. Transformation of Polyethylene

The liquefaction of polyethylene has been reported by Enomoto et al., which demonstrated that the transformation occurred at around at 400-450°C with supercritical water. Shown in Fig. 9 is a relation between viscosity and degree of filling of water in vessel (corresponded to density and pressure). Maximum viscosity is attained near the critical volume (30-40%), but it has extremely lower values at 20% of filling ratio. The GC-MS spectra of products in various conditions of degree of filling and temperature are shown in Fig. 10. The products consisted of paraffin with C$_8$-C$_{20}$ and at the lower filling ratio and higher temperature, the formation of low molecular weight material was observed. These results in supercritical region reveal that the decomposition of low molecule products may occurs in the zone of lower pressure and higher temperature, that is, at lower dielectric constant values. As mentioned above, high density water (high pressure and degree of filling) shows a high dielectric constant and acts as a suitable reaction media for ionic reaction. However, low density water (lower pressure and degree of filling) is considered to be a successful media for organic reaction. The characteristics of hydrothermal solution as

| Sample | Solvent | Temp. [°C] | Total gas [ml] | CH$_4$ | C$_2$H$_6$ | C$_3$H$_8$ | C$_4$H$_{10}$ | CO$_2$ | H$_2$
<table>
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<td>3.6</td>
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415°C, Reaction time; 3 h.

Fig. 9 Viscosity of Product Oil from Polyethylene as a Function of Filling Ratio Temperature

Comparisons among those of degree of filling; 20, 40 and 60% and of reaction temperatures; 400, 415 and 450°C.

Fig. 10 GC-MS Chromatograms of Products from Polyethylene
reaction media can be continuously changed by varying the P-T conditions to suit every reaction media from ionic to radical reaction, may be a possibility to successfully treated organic wastes.

4.2.3. Liquefaction of Vulcanized Rubber

Vulcanized rubber (Table 2) can be easily transformed into a liquid using high temperature and lower pressure conditions (420°C, up to 20 MPa) as shown in Fig. 11. As it can be seen from this figure, the results show a similar transformation behavior as in the case of polyethylene, in other words, same oily products in same conditions. In addition, the sulfur content in oily products were extremely low and the zinc sulfide formed separately as a precipitate in water phase. These results represent the possibility to use this process for the desulfurization of petroleum products.

5. Continuous Flow System Tube Reactor

Shown in Fig. 12 is a continuous flow tube reactor for hydrothermal treatment. The main characteristics of hydrothermal process are in extremely high reaction velocity and wide selectivity as a reaction media. The wide selectivity as reaction media is commonly difficult to obtain by using batch type autoclave in conditions of saturated vapor pressure. The continuous flow pipe line system with high pressure liquid was developed. The first studies were carried out on synthesis of ammonia by Harber-Bosch process, and liquefaction of coal by Bergius process, before the World War II. The pipeline system for oil refineries was recently developed. The hot water pipeline system using pure water was developed for atomic power plants, and the system containing some ions and slurry was developed for wet metallurgy. The system under supercritical water conditions for the treatment of slurry is yet to be developed, because of high corrosion limitation requirement and defect found in basic data.

On the other hand, there are much potential requirement for tube reactor hydrothermal process utilizing, in frontiers of advanced material formation, metallurgy, new energy transformation technology, recycle system from waste to products, and treatment of toxic and hazardous materials. Recently, new sensors and tough alloys such as Hastelloy, Inconel, Stellite, etc. incorporating computer control systems have been under evaluation. The heating with small diameter tubes provides advantages in the form of low process cost, safety, closed system, not requiring large space, disposable corroded parts and micro control system for pressure valve and pump making P-T selectivity simple and reliable.

6. Conclusion

The hydrothermal solution conducted in conjunction with high temperature and pressure water system is a suitable reaction media to conduce almost all reaction media.
from ionic to radical, controlling the P-T conditions, species and concentration of solute.

A bond with maldistributed electrons, that is, the hetero-organic compound, is easily decomposed in the liquid phase by using saturated vapor pressure at a high pressure region in supercritical conditions. Conditions for decomposition of organic polymer with covalent bond exist in the vapor phase in saturated vapor pressure, and in the low pressure site in supercritical region.

Considering a slurry transformation using heating small diameter tube, new process which combines the reaction and separation might be expected to be used as a new recycle system containing waste treatment and new material formation.

References