

FUEL PRODUCTION BY RAPID HYDROLYSIS OF POLYMERIC MATERIALS

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Abstract

Rapid pyrolysis and rapid hydrolysis are used as parts of hydrogasification. Hydrogasification has been developed to produce methane (SNG) directly from coal. Reaction conditions of hydrogasification are at around 1000K and 7MPa, expected products are methane and BTX. Only coal had been thought to use for hydrogasification process, co-feed of waste plastics with coal was considered to diversify feedstock. We had studied the hydrogasification of polyethylene (PE) and coal/PE mixture. Hydrogasification of coal/PE mixture was carried out and the methane yield was compared to the yield from hydrogasification of coal and PE respectively. In conclusion, the synergistic effect on methane yield was found by sample mixing. The mixing effect of coal/PP was similar to that in coal/PE mixture. Rapid hydrolysis of biomass tar and epoxy oligomers' model compounds was also carried out. Difference in the mixing effect which depended on the samples was discussed. The mixing effect was found by using some mixture of the model compounds, but was not found for some other mixtures. The effect was smaller than that of the coal/PE mixture.

Keywords: rapid hydrolysis, coal, plastics, biomass, mixture

1. Introduction

In the study of co-hydrogasification of coal/plastic mixture, we had found the synergistic effect for the increase in methane production [1]. The effect was investigated by various conditions of experimental research. Rapid pyrolysis and rapid hydrolysis of polymeric materials and their model compounds were carried out. In this paper, several R&D work for fuel production were described, the experimental results were discussed and were summarized. Difference in the synergistic effect was found among the several mixture systems containing each two components and the factor of the effect was discussed.

2. Co-hydrogasification of coal/plastics

Hydrogasification has been developed to produce methane (SNG) directly from coal. Hydrogasification reaction mainly consists of rapid pyrolysis and rapid hydrolysis which is reaction with hydrogen. Methane is a main component of natural gas. Demand for natural gas is increasing because of its high environmental acceptability. There are a couple of ways to produce SNG, one is a direct method such as hydrogasification and the other is an indirect method through synthesis of CO/H₂ produced by gasification. Theoretical energy efficiency for direct method is higher than that for indirect method.

Only coal had been thought to use for hydrogasification process, co-feed of waste plastics with coal was considered to diversify feedstock in Japan. We had studied the hydrogasification of polyethylene (PE) and coal/PE mixture [1]. Hydrogasification of coal/PE mixture

was carried out and the methane yield was compared to the yield from hydrogasification of coal and PE respectively. Reaction conditions of hydrogasification were at around 1073K and 7MPa. The value was calculated from the results obtained from coal and PE, respectively, to estimate the methane yield from the mixture assumes no mutual influence. The experimental result of methane yield from the mixture was obviously greater than the value calculated, especially for the short reaction time of 2–3s. It suggests that a significant synergistic effect was present in co-hydrogasification of coal/PE. Enthalpy generated by hydrogasification of PE is larger than the heat required to compensate for the endothermic process caused by the pyrolysis of coal. Enhanced reactions caused by the exothermic process may result in the synergistic effect. In recent study, it was suggested that not only coal reaction but also PE reaction seemed to be enhanced [2]. Polypropylene was also used as sample for co-hydrogasification. As a result, the mixing effect in coal/PP for methane production was similar to that in coal/PE mixture. Moreover, positive effect for increase in methane production was also found in the hydrogen partial pressure of 0.9MPa. Therefore, the synergistic effect was observed in coal/plastics co-hydrogasification for several kinds of plastics and for wide range of hydrogen pressure.

3. Production of Fuel from wood biomass waste containing synthetic polymer

A new process, consistent with the several process components, had proposed to produce a fuel from wood wastes mixed with synthetic polymer materials such as

plastics or adhesives [3]. The process components are as follows:

Pyrolysis - Wood wastes mixed with synthetic polymers pyrolyzed and degraded to lower molecular weight products at mild conditions.

Hydrogen production - The solid residue produced from the pyrolysis reactor is converted to hydrogen under coexistence of water and the sodium compound.

Cracking/reforming - The liquid heavy compounds, tar, produced from the pyrolysis reactor is cracked and reformed by hydrogen to light hydrocarbons. The light hydrocarbons would mainly be methane, ethane, and benzene. Elements such as nitrogen and chlorine could be separated as valuable materials such as ammonia and hydrogen chlorides.

In the cracking/reforming process component, rapid hydrolysis is adopted and raw materials are mixtures of various sorts of hydrocarbons. For rapid hydrolysis of such mixtures, similar effect to synergy in co-hydrogasification of coal/plastics was thought to be expected. Model compounds, paraffin, naphthalene and phenol as biomass tar were used to examine the mixing effect [4]. As a result, the increase in product yield on reaction with mixing were observed for phenol/paraffin mixture even the change was smaller than that in co-hydrogasification of coal/plastics. For the mixture of phenol/naphthalene, the mixing effect was negative. The reason why the mixing effect is to be occurred seems that exothermic reaction promotes endothermic reaction in a short time.

4. Rapid pyrolysis of oligomers' model compounds from resin and biomass tar

To recover useful materials from glass-fiber composite epoxy boards, such as those found in end-of-life electronic equipment, we have proposed a new process that involves liquefying the epoxy resin under mild conditions using heavy tar derived from pyrolysis of woody biomass [5]. In this process, liquefied and partially pyrolyzed epoxy resin oligomers along with the heavy tar are reformed to lighter materials. These lighter materials can then be used as the circulation solvent for the proposed process or as feedstock for fuel or chemicals. As an experimental study, we reformed model compounds in a pressurized hydrogen atmosphere. The mixture of phenol and bisphenol-A was used. As a result, the experimental methane yield from the mixture was smaller than the calculated yield [6, 7]. These phenomena are different than those observed for hydrolysis of a mixture of phenol/paraffin (section 3) and for hydrogasification of a mixture of coal/plastics (section 2) [1, 4]. These studies suggested that the enthalpy from paraffin or PE hydrogenation, which is an exothermic reaction, promoted the endothermic reaction of phenol or coal, respectively. From the deviations in temperature during rapid hydrolysis of phenol, bisphenol-A, and their mixture, an endothermic reaction dominated for all samples in the early stage of the reaction. Therefore, it seems consistent that the methane yield from the mixture

of phenol and bisphenol-A was not increased by mixing, but rather decreased as a result of this endothermic process.

5. Conclusions

Rapid pyrolysis and rapid hydrolysis of coal, plastics, biomass tar and epoxy oligomers' model compounds were carried out. Useful fuel could be produced from various kind of polymeric materials by rapid pyrolysis and rapid hydrolysis. Difference in the mixing effect which depended on the samples was discussed. The synergistic mixing effect was found by using some mixture, but was not found for some other mixtures. The synergistic effect for methane production by co-hydrogasification of mixture was present when the enthalpy generated by rapid hydrolysis of one component is larger than the heat required by the pyrolysis of the other component. The effect may not be presented or be negative when the both components of the mixture show similar phenomena of endothermic pyrolysis processes.

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