

# Simulation of Organic Reactions in the Submarine Hydrothermal Systems by Supercritical Water Flow Reactor

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A number of studies have been performed to synthesize organic compounds in simulated hydrothermal vent systems. Closed furnaces were, however, used in most of the studies. Actual hydrothermal vents can be considered flow reaction systems, where sea water can be heated over the supercritical point. So we constructed a supercritical water flow reactor ( SCWFR ) to investigate the possible organic reactions in SHVs and their possible roles in generation of life.

A mixture of KCN ( 0.1M ), HCHO ( 0.1M ) and  $\text{NH}_4\text{HCO}_3$  (0.05M ) was pumped into the SCWFR. A wide variety of organic compounds including amino acids detected at 50-400 deg. cel. by cation exchange HPLC. Glycine, alanine etc. were detected. Further works are in progress to test the effects of pH, red-ox potential and roles of metal ions.

Reducing conditions are more favorable for abiotic synthesis of organic compounds than the non- or mildly reducing conditions. Submarine hydrothermal vents ( SHVs ) preserves reducing environments even in the present oxidizing earth environments. A number of studies have been performed to synthesize organic compounds in simulated hydrothermal vent systems. Closed furnaces were, however, used in most of the studies [1,2,3]. Actual hydrothermal vents can be considered flow reaction systems, where sea water can be heated over the supercritical point. So we constructed a supercritical water flow reactor ( SCWFR ) to investigate the possible organic reactions in SHVs and their possible roles in generation of life [4].

Instrumentation of the SCWFR consists of the following major parts. Aqueous solution containing starting materials are pumped into an infrared gold image furnace, where the solution can be heated even more than 1500 deg. Cel. within a few seconds. Heating of the furnace is controlled by programmed controller. Temperature of the fluid inside the reaction tube and surface temperature of the reaction tube can be monitored with thermocouples, which are associated with the controller. Pressure inside the tube is controlled with a back pressure regulator independently from the temperature. The sample can be quenched in a cold bath just after heated.

A wide range of temperatures ( 50-600 deg. Cel. ) have been applied to perform reactions through the SCWFR. The heat distribution rate to the fluid inside the reaction tube differs with the temperature difference on the outer surface of the reaction tube. For example, at the lower temperature range  $>350$  deg. Cel, the outer surface or set temperature of the reaction tube is higher than the fluid temperature inside of the reaction tube. On the other hand, at  $<350$  deg. Cel. the scene become just opposite to the previous conditions. The heat distribution also differs for the flow rate of the fluid. The difference between outer surface temperature of the reaction tube and fluid temperature is lesser in case of higher flow rate than that of lower flow rate.

Three types of experiments were being performed by SCWFR. Those are as follows. Firstly, only glycine solution was heated up to supercritical conditions of water. The cation-Exchange chromatograms obtained from the sample under supercritical conditions showed some new peaks before the retention time of aspartic acid. Those products are under determination.

Secondly, Strecker type reactions at higher temperatures were examined. A mixture of KCN (0.1M ), HCHO ( 0.1M ) and  $\text{NH}_4\text{HCO}_3$  ( 0.05M ) was pumped into the SCWFR. The products were determined by cation exchange HPLC after acid hydrolysis. Only glycine was detected at 50 deg. Cel. in the product. When the reaction temperature was increased, alanine (  $>100$  deg. Cel. ), sarcosine (  $>150$  deg. Cel. ), beta-alanine, gamma-aminobutyric acid, 5-aminovaleric acid and 6-aminocaproic acid (  $>300$  deg. Cel. ) were detected.

Thirdly, serine and imidazole were reacted at 150-400 deg. Cel.. Glycine , alanine and alpha-aminobutyric acid were detected prominently together with many other unidentified compounds in the product.

The products obtained from the above experiments showed that a wide variety of organic compounds including amino acids could be formed in hydrothermal systems. Further works are in progress to test the effects of pH, red-ox potential and roles of metal ions.

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## References :

1. Hiroshi Yanagawa, Kensei Kobayashi, *Origins life Evol. Biosphere*, 22, 147-158 ( 1992 ).
2. William L. Marshall, *Geochimica et Cosmochimica Acta*, 58(9), 2099-2106 ( 1994 ).
3. R.J.C. Hennet, N.G. Holm, M.H. Engel, *Naturwissenschaften* 79, 361-365 ( 1992 ).
4. Md. Nazrul Islam, Takeo Kaneko, Kensei Kobayashi *Viva Origino*, 28(1), 9 ( 2000).