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A MULTI-SAMPLE, PROGRAMMED-HEATING, AND RAPID-QUENCH APPARATUS FOR CONFINED OR MSSV PYROLYSIS

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Abstract

A new hydrothermal apparatus has been developed to improve the efficiency of conventional techniques by simultaneously heating multiple reactant samples at programmed heating rates under pressure, and allowing individual sample to quench automatically at desired times along the heating profile without interrupt the experiments. The apparatus have been preliminarily tested at heating rates ranging from 0.1 °C/min to 30 °C/min up to 600 °C, and pressure have been tested up to 30 MPa. The ranges of pressure, temperature and heating rate can be improved through further development. The apparatus is particularly useful for kinetic study of oil and gas generation or oil cracking under pressures, which usually requires many series of labor intensive and time-consuming experiments, such as confined gold-tube pyrolysis. A simplified version of the apparatus, which was modified to operate at one atmosphere pressure, may be used to effectively perform Microscale Sealed Vessel (MSSV) experiments. For comparison with the available closed system pyrolysis techniques, this study reviews briefly the capability and limitations of each technique.

Keywords: Pressure reactor, programmed heating, hydrous pyrolysis, confined pressure pyrolysis, microscale sealed vessel, kerogen maturation, oil kineitcs

1. Introduction

Hydrothermal apparatus have been used to perform a variety of experiments for both academic and industrial research. Geoscientists used pressure vessels for performing experiments and researches in mineralogy and geochemistry (Ulmer and Barnes, 1987). The vessels are used to expose geological samples to pressure and temperature conditions to test theoretical predictions and simulate the results of natural geological processes, such as measuring mineral stability, solubility and reaction kinetics, clay transformation kinetics, and fluid-rock interactions. Such pressure systems have also been previously used in the synthesis of materials, determinations of stability and phase relationships of various materials, pressure-volume-temperature studies, determinations of material solubility, high pressure differential thermal analyses, accelerated corrosion testing, special environmental testing, crystal growth etc. (Somiya, 1989; Ulmer and Barnes, 1987; Sanchez et al., 1998). Recently the system, in particular, the confined pressure technique, has been increasingly applied to the study of the closed system pyrolysis for oil/gas generation and cracking kinetics and yields under subsurface pressure conditions with and without water (e.g. Monthioux, et al., 1988; Domine, 1989. Landais et al., 1994; Hill et al., 1994; Seewald, 1994; Michels et al., 1995a,b; Freund et al., 1993; Burnham, et al, 1995a,b; Jackson, et al., 1995; Behar, et al., 1997ab; Huang, 1996a; Burnham, et al, 1997; Torre, et al., 1997; Vandenbroucke, et al., 1999). The merit of the confined system, which normally uses deformable capsules or bags made from gold or other noble metals, is to confine the reactants within the sample (Monthioux, et. al., 1985). It is believed to better simulate organic reactions under subsurface conditions (Monthioux, et al., 1985; 1986; Michels et al., 1995a,b; Behar, et al., 1997a,b). It enables us to study the effect of confined pressure on the organic reactions (Domine, 1989; Mallinson, et al., 1991; Landais et al., 1993; Michels et al., 1994; 1995a; Freund et al.,1993; Huang, 1996a; Hill et al., 1994; Torre, et al., 1997), and therefore better simulate organic reactions at a variety of geological conditions.

The conventional apparatus for confined pyrolysis such as cold-seal pressure vessel, however, was restricted by its inefficiency in operation, and by inability to run controlled-heating experiments due to large thermal mass of the vessel. A new pyrolysis reactor (Huang and Otten, 2000) with internally heated-capability has been developed to improve the efficiency by simultaneously heating multiple reactant samples at programmed heating rates under pressure, and allowing individual samples to quench automatically at desired times along the heating profile without interrupting the experiments. This paper reviews and compares the merits and limitations the new apparatus with the conventional techniques used for the closed-system pyrolysis, presents the conceptual design of the new apparatus, and describes the detailed fabrication and some experiences gained based on preliminary testing for a pilot apparatus.

2. Selecting pyrolysis techniques

Pyrolysis techniques have been widely used in charactering and simulating organic reactions, including oil and gas generation, oil cracking and others. Previous studies show that simulating results highly depend on the experimental conditions and pyrolysis technique. The comparison of the results obtained among different pyrolysis techniques and natural observations were previously reported (Monthioux et al., 1986; Comet, et al., 1986; Price and Wenger, et al., 1992; Landais, et al., 1994; Andresen et al., 1995; Ritter et al., 1995; Barth, et al., 1996; 1996; Behar, et al., 1997b; Lewan, 1997; 1998a; Burnham, 1998). The proper selection of the techniques is, therefore, essential to the success of the studied program. The criteria of selection include (1) open vs. closed system, (2) anhydrous vs. hydrous, (3) maximum pressure and temperatures, 3) confined vs. unconfined (i.e. with head space), (4) isothermal vs. programmed heating, (5) quenching rate, (6) online vs. offline analysis of pyrolysates, and (7) efficiency to operate. In this review some of these criteria in the closed system pyrolysis are discussed, with special emphasis on the pressure vessel for the pyrolysis.

2.1 Vessels for closed-system pyrolysis

Conventional pressure vessels used to perform hydrothermal experiments in closed system includes fixed -volume autoclave (Morey and Fournier, 1961; Bourcier and Barnes, 1987), rocking autoclaves with gold bag (Dickson et al., 1963; Seyfried, et al., 1979, 1987), cold-seal pressure vessels (Tuttle, 1949), internally heated vessels (Holloway, 1971; Lofgren, 1987), internally heated rapid-quench vessel (Holloway, et al., 1992), piston-cylinder apparatus (Boyd, et al.,1967), hydrothermal diamond anvil cell (Bassett, et al., 1993), flow-through reaction cell (Barnes et al., 1972; Potter, et al., 1987), and the like. The details of the apparatus and experimental techniques for hydrothermal experiments were reviewed and summarized in Ulmer and Barnes (1987). Most of these pressure vessels were originally designed for the hydrothermal experiments in the study of petrology and mineralogy. Recently these types of equipment have been increasingly used for the study of the anhydrous and hydrous closed-system pyrolysis of organic matter. In order to select the most suitable pyrolysis technique for specific objectives of the studied experiments, we need to be aware of the merits and limitations of each technique. The followings are brief reviews of the capabilities, applications as well as the merits and limitations of the commonly used techniques in the studies of organic pyrolysis (Table 1).

2.1.1. Hydrous pyrolysis

The fixed-volume autoclave (e.g. Parr-type vessel) is by far the most commonly used apparatus for the pyrolysis study of organic reactions, in particular, for hydrous pyrolysis (e.g. Lewan, 1983, 1985; Winters et al., 1983; Barth et al, 1989; Landais, et al., 1994). Although the term "hydrous pyrolysis" has been generally used for any pyrolysis technique involving water, it has been increasingly assigned to a specific pyrolysis technique. The hydrous pyrolysis, in the strictly sense, is a pyrolysis technique with which organic sample with water contained in a rigid autoclave was heated at temperatures less than the critical point of water (373 °C) for a desired run time; this technique requires the solid sample entirely submerging in liquid phase of water at the pyrolysis temperatures (Lewan, 1993). As the role of water in the generation of petroleum has been increasingly recognized (Hoering, 1984; Siskin and Katritzky, 1991; Lewan, 1997), the hydrous pyrolysis technique is believed to properly simulate oil/gas generation and expulsion from source rocks (Barth et al., 1994; Lewan 1997; Seewald et al., 1998; Ritter, et al., 1995; Schimmelmann, et al., 1999). It has been most commonly used to simulate the oil and gas generation and study their kinetics (e.g. Lewan, 1985, 1993, 1997; Burnham et al., 1988; Barth et al, 1989, 1994; Nielsen and Barth, 1991; Ritter, et al., 1993b; Barth and Nelson, 1993; Burnham et al., 1995a). Recently, the study has focused on the determination of the stability and transformnation kinetics of biomarkers (Lewan et al., 1986; Comet et al., 1986; Peters et al., 1990; Marzi et al., 1990; Abbott et al., 1990; Ritter et al., 1993a; Koopmans, et al., 1996; Abbott, et al., 1995; Koopmans, et al., 1995, 1998a, 1998b; Damste, et al., 1998; Stalker et al., 1998; Koopmans, et al., 1999; Barth, 1999). Other applications of this technique include the pyrolysis of crude oil (Curiale, et al., 1992; Karaka, et al., 1993), the oil-source rock correlation (Waseda et al., 1996; Clegg et al., 1998), fractionation of carbon, hydrogen and oxygen isotopes during oil and gas generation (Lewan, 1983; Hoering, 1984; Andresen, et al., 1993, 1995), the reservoir geochemistry (Magnier and Huc, 1995), organic sulfur geochemistry (Song, et al., 1998; Koopmans, et al., 1998b), hydrogenation and oxidation of coals and kerogen (Stalker, et al., 1994; Landais and G?rard, 1996; Sugimoto, 1997; Everlien, 1998), organic acids generation and their stability (Eglinton et al., 1987; Andresen, et al., 1994; Lundegard and Senftle, 1987), and others. In addition, the technique has provided useful information for the study of retention and migration of oil and gas

(Lewan, et al., 1995; Mishra, et al., 1996). Although this technique runs routinely only in a closed-system, it has been improved to conduct open-system hydrous pyrolysis, where gas, oil and water in the pyrolysates were extracted from the autoclave during experiments or transferred to an additional pressure vessel during an experiment. Alternatively, the open-system hydrous pyrolysis can be done by flashing the hydrothermal water through a source rock using the water-flow pyrolysis technique (Rudkiewicz, et al., 1994; Korzhov et al., 1996; W. L. Huang and G. A. Otten, umpublished). The fixed-volume autoclave can perform anhydrous pyrolysis in a closed system, either with or without inert gas pressure (Smith et al., 1994; Lewan, 1997; Koopmans et al., 1998a); the heating may be conducted in sand bath to minimize the temperature gradient within the autoclave during anhydrous pyrolysis without inert gas, (Lewan, 1998b).

There are some limitations, however, for the hydrous pyrolysis. First, the presence of head space for vapor phase in the sample chamber may cause the preferentially partition of light pyrolysates into vapor phase and prevents further reaction with residual sample. This limitation can be reduced using flexure container, such as gold bag used by the rocky autoclave (Seewald, 1994). Secondarily, the hydrous pyrolysis is routinely run only at the vapor pressure of water. The limitation has been improved by the high-pressure hydrous pyrolysis technique, which has been performed by adding extra-pressure using an inert gas in addition to water vapor (e.g. Price and Wegner, 1992; Landais, et al., 1994, 1995b; Kevenvolden, et al., 1994). The presence of the inert gas, however, creates an unrealistic condition that does not occur in nature. The other limitation includes the likely contaminant reactions or catalytic effect between sample and the vessel materials (e.g. stainless steel), particularly in solution rich in organic acids (Palmer and Drummond, 1986; Karaka, et al., 1993). The Titanium or Hastelloy autoclave or gold-plated or glass-lined autoclve have been used to minimize the catalytic effect and the contaminations (Curiale, et al., 1992; Palmer and Drummond, 1992). The sealed Pyrex glass tubes (Huizinga, et al., 1987) or sand pack (Mishra et al., 1996) inserted into the stainless steel autoclave are alternative ways to prevent sample from contacting with metallic walls. However, for most organic experiments without significant amounts of organic acids, the stainless steel autoclave is practicable so long as the internal surface of a new vessel was oxidized or carburized or coated by graphite after several preliminary experiments (Barth et al, 1989; Lewan, 1993). The hydrous pyrolysis is routinely performed only at isothermal condition because the large thermal mass of the vessel prevents proper control of high heating rates. The progressive heating experiments have been conducted using programmed step heating (Andresen, et al., 1995).

2.1.2. Confining pressure pyrolysis

The confined pressure pyrolysis was performed using flexure containers, which can be deformed to adjust the sample pressure to equal the externally applied pressure. The source rocks or crude oil with or without water were sealed in capsules or bags made from gold or other noble metals. The system minimizes the free vapor space and confines the reaction products within the sample for further reaction (Monthioux, et al., 1985), and therefore simulates closely the lithostatic or hydrostatic condition at subsurface. Although the confined pressure pyrolysis was conducted routinely for organic sample without added water, gold-tube experiments enable us to add water or other liquid phases (Huang, 1986). It can be done under controlled redox conditions using mineral buffers (Eugster, 1957; Barnes, 1987; Seewald, 1994). In principle, any pressure vessel can be used to run the confined system pyrolysis so long as the flexure containers are used. The cold-seal pressure vessel, which was made from of a high strength alloy material and used gold tubes as sample containers, is capable to run pyrolysis at high pressures (up to 300 MPa) and temperatures (800 °C). It is the most commonly used confined pressure pyrolysis technique for studying a vareity of organic reactions (e.g. Monthioux, et al., 1985; Monthioux and Landais, 1989; Landais, et al., 1989; Garrigues et al., 1990; Blanc and Connan, 1992; Freund et al., 1993; Landais et al., 1994; Michels et al., 1994; Michels et al., 1995b; Mansuy and Landais, 1996; Landais, 1996a, 1989, 1994; Hill et al., 1994; Andresen et al., 1998). A quench-devise can be installed for rapidly quenching the sample within the vessel (Wellman, 1970; Monthioux, et al., 1985; Huang, et al., 1986; Freund et al., 1993). The gold-tube experiments can be extended to very high-pressure (up to 1500 °C and 3.5 GPa) using the solid-medium piston-cylinder apparatus (Domine, 1989; Torre, et al., 1997). The limitation for coal-sealed and piston-cylinder apparatus include small sample size for chemical analysis of the pyrolysates, and relatively time-consuming for running individual sample. A modified gold-tube experiments (IFP-type, Fig. 4 in Behar, et al., 1991b) using multiple gold tubes in a larger fixed volume vessel is more efficient than cold-seal vessel but is limited to lower temperature (max. 700 °C) and pressure (max. 100 MPa but routinely at around 15 MPa). The kinetic parameters for the oil and gas generation and cracking have been determined from this technique (Behar, et al., 1997b; McKinney et al., 1998; Vandenbroucke, et al. 1999; Behar and Vandenbroucke, 1996; 199a,b; Tomic et al., 1995; Behar and Hatcher, 1996; Behar, et al., 1997a; Behar et. al., 1991a,b). These multiple sample capability of IFP technique, however, is limited because all samples must be conducted together at same temperature, pressure and quench in the same run duration. This technique can be improved by the newly designed multi-sample pyrolysis technique reported in this study.

Another type of the confined pressure technique, the rocking autoclave, has the capability to monitor the change of fluid composition during the experiment. The technique uses flexure gold bag as sample container, which is sealed by an exchangeable Titanium head equipped with a sampling devise. This devise enables us to sample the fluid and gas during the course of an experiment without interrupting the experiment. It has been successfully used for the study of the organic reactions (Seewald, 1994; Manning, et al., 1991; Knauss et al., 1992) or oil cracking kinetics (Mallinson, et al., 1991; Jackson, et al., 1995; Burnham, et al, 1995a). It, however, is restricted by its maximum temperature (up to 400 °C at 20 MPa), and the difficulty to operate. It is also limited by the frequent failure due to the rupture of the gold bags caused by the gas pressure generated during organic pyrolysis. The latter problem can be avoided by properly control the amounts of reactants and water used.

2.1.3. Microscale Sealed Vessel (MSSV)

The Microscale Sealed Vessel (MSSV) pyrolysis technique (Horsfield, et al., 1989) provides an efficient way to study the oil generation and cracking kinetics (Horsfield, et al., 1991; Schenk and Horsfield, 1993, 1996, 1997; Schenk et al., 1997a, b; Boreham et al., 1999; Ritter, et al., 1995; Stott and Abbott, 1995; Dieckmann et al., 1998). This technique uses Pyrex-glass micro-tubes (or silica tubes at > 550 °C) as sample containers heated in an oven. The merits of this method in organic pyrolysis include its simplicity and ease to practice, its capability to run at programmed heating rates, and its efficiency to online crash the micro-tube for analyzing pyrolysates using gas chromatograph (Horsfield, et al., 1989; 1991). This technique is particularly useful for the measurement of oil generation and cracking kinetics in closed system (Dieckmann et al., 1998). The technique, however, requires plenty of attention to remove the sample tubes timely, and therefore is inconvenient for overnight experiments. In addition, the opening of the oven may disturb the temperatures of the rest of samples. These limitations can be significantly improved by adopting an automatic sampling devise presented in this study. In addition, the presence of dead space within the micro-tubes and inability to run sample in the presence of water, and at subsurface pressure. Nevertheless, these may not be a severe limitations in mimiking natural oil generation and cracking processes as discussed in Schenk et al., (1997b). Similar technique with large size of Pyrex glass or silica tube was performed for the study of the reaction of sulfides (Kullerund, 1971) and for organic pyrolysis study (Harwood, 1977; Abbott et al., 1985a, 1985b; Tannenbaum and Kaplan, 1985; Huizinga et al., 1987; Kagi, et al., 1990; Tang and Stauffer, 1995). A BP's proprietary pyrolysis technique uses sealed platinum capsules as sample container, which at the end of each experiment were burst in the injector of a GC for the online analysis of the effluent (Quigley and Mackenzie, 1988). The technique is able to run programmed pyrolysis. It is not clear if the external pressure was applied on the platinum capsule during the heating in this technique. The diffusion of hydrogen out of the platinum capsule at the pyrolysis temperatures may be significant (Chou, 1986), and may affect the reaction pathways of the organic reactions. The substitution of platinum by gold, which has much lower permeability to hydrogen, is suggested.

2.1.4. Diamond Anvil Cell (DAC) pyrolysis

The hydrothermal Diamond Anvil Cell (DAC) provides a unique tool for the visualization of oil generation and cracking (Huang, 1996b; Wong and Huang, 2001), and in-situ monitoring organic reactions rates using spectroscopy during pyrolysis (Huang, and Otten, 1998; 2001). The merits of this technique include (1) *in-situ* visualization of the organic transformation of sample during pyrolysis; this is particularly useful for distinguishing the oil-prone from gas-prone source rocks or coals (Wong and Huang, 2001). (2) experiments with solid and fluids (e.g. crude oil and water) (3) *in-situ* monitoring of the reaction progress for kinetic study using spectroscopy (e.g. fluorescence, infrared, and synchrotron radiation etc.). (4) accurately measurement of the sample temperatures, and wide range of heating rates and temperature (up to 1000 °C) and pressures (up to 1 GPa). However, very small sample size used in this technique, although having some advantages, limits its applications only to homogeneous sample; more duplicated runs should be done for reducing the uncertainty caused by the heterogeneity of the sample. While the low analytical resolution of the spectroscopic analysis relative to GC-MS may be a limitation, its ability to characterize solid organic matter may reveal chemical functionalities of the samples. This technique is still in developing.

2.2. Isothermal vs. controlled heating rate experiments

Other important factor in selecting the suitable apparatus for pyrolysis is the way sample heated during experiments. The major differences between the conventional inorganic and organic experiments are the heating and quenching processes. Most inorganic reactions were conducted in isothermal conditions whereas most organic pyrolysis experiments, in particular for the kinetic determination, were preferentially conducted in controlled-heating process. Most organic reaction experiments require higher quench rate than inorganic reactions because of the faster rates of the back reactions during quenching. Application of the hydrothermal vessels, which originally designed for isothermal experiments, to the study of organic reaction kinetics is limited if the controlled-heating is required. Most of the previous pressure vessels including cold-seal type, rocking autoclave and hydrous pyrolysis are usually adopted for runs only at isothermal conditions or slow heating rates. The incapability to run controlled-heating for these experiments is hard to overcome due to the large thermal mass of the pressure vessel. Additionally, these vessels are limited by slow rate of sample quenching. Internally heated vessel (Holloway, et al., 1992) provides improved control of the heating and quenching rate of the sample since only the interior space in the vessel is heated thus eliminating the need to heat the entire mass of the vessel itself. However, the vessel limits to one sample in each experiment. Microscale Sealed Vessel (MSSV) pyrolysis technique, sealed Platinum capsule technique, and IFP gold tube experiments provide the capability to control the heating rate. The maximum heating rate used in the IFP technique may be limited due to the large thermal mass of the pressure vessel.

2.3. Multi-sample capability

Pyrolysis experiments usually require that the relevant experimental processes be performed repetitively. Repetitions of these tests may be performed at the same, or different, pressures and temperatures and in both cases, for varying periods of time. A common limitation of existing systems in performing such experiments on a repetitive basis is that these systems are designed to run only one sample at one set of pressure-temperature-time conditions. The systems of hydrous pyrolysis, and cold seal vessel are only adapted for use with individual reactant samples whereas Parr and rocking type vessel permit to sample only solutions but not solid in the course of experiments. This limitation results in significant manpower requirements in order to prepare each sample and each experiment individually for sampling solid products. Furthermore, limitations on available time for obtaining desired results may dictate the need for multiple pieces of test equipment in order to run numerous tests in parallel instead of in series. The requirement of the multi-sample experiments is particularly important for the study of organic reaction kinetics, which commonly conducted at different heating rates while sampled sequentially at different time (or temperature) along a heating profile. Accordingly, in order to reduce the total time required for multiple tests and to reduce both the manpower and equipment costs associated with multiple tests, a need exists for equipment capable of simultaneously performing experiments upon multiple samples while varying testing conditions of pressure, temperature, and/or time. Microscale Sealed Vessel (MSSV), IFP gold tube technique and the present apparatus provide the capability to run multi-samples.

3. Concepttual design of the apparatus

The present apparatus includes a pressure vessel capable of simultaneously subjecting multiple reactant samples to controlled pressure and temperature conditions, in particular, at controlled heating rates. Each individual sample can be rapidly cooled at a desired run time while the other samples continue running under the pressure and temperature. Typically, the apparatus includes a fix-volume pressure vessel (e.g. Parr type) having both a hot zone and a quench zone inside the vessel (Fig. 1). The hot-zone is composed of a coil resistant-heater and a sample holder capable of holding ten or more sample capsules. Each individual capsule can be rapidly cooled at a desired run time while the others continue running under the pressure and temperature; it is equipped with means for selectively dropping individual capsules from the holder to the quench-zone at a time or times determined by the operator. The internally heated device reduces the size and the thermal mass of the heater and therefore provides better control of heating rate. In a preferred embodiment, the hot zone is located above the quench zone. Multiple reactant samples can be held in individual chambers in the holder by a sample retaining support. The chambers are arranged in a circular pattern around a generally vertical axis. The holder and the support are mounted to allow rotation with respect to one another about this axis. The support is provided with at least one opening that sequentially aligns with each of the chambers during this rotation, allowing individual samples to drop from the holder to the quench zone. The quench zone can be created by an external cooling devise, such as cooling jacket or water bath. A simplified version of the apparatus, which was modified to operate at one atmosphere pressure, may be used to effectively perform Microscale Sealed Vessel (MSSV) experiments.

4. Detailed description of the apparatus

The multi-sample pressure vessel, as illustrated in Figure 2 and described in the text below, is adapted for experiments to be performed on multiple test samples. Figure 1 shows one embodiment of the reactor. A pressure vessel defines an interior cavity. Closure and the pressure seal of the vessel are provided by well-known and conventional means. In this embodiment, all components of the pressure vessel that must pass through the vessel wall are provided with sealed entry holes through the pressure head. The vessel shown in Figure 2 is Parr Instrument Company

Model243HC5 of Hastelloy C-276 construction. However, the vessel may be fabricated from any material capable of withstanding the required design operating temperature and pressure. The interior cavity as shown contains two distinct temperature regions, a hot zone and a quench zone. In the embodiment shown, the hot zone is located above the quench zone. Pressure is provided and maintained in the pressure vessel by a gas booster compression system. In the embodiment shown in Figure 1, a sample holder is mounted in a fixed position within the hot zone.

The sample holder contains a plurality of sample chambers arranged in a circular pattern about a generally vertical axis of rotation. The chambers in the embodiment of the pressure vessel shown in Figure 1 are cylindrical holes having generally vertical longitudinal axes. A sample retaining support is provided to prevent samples from falling from the sample holder into the quench zone. In Figure 1, the support is shown as a flat plate ratably mounted in close proximity to a flat surface on the underside of the sample holder. The sample holder and support as shown in Figures 1, 2A, and 2B are custom fabricated to the desired dimensions from 316L grade stainless steel bar stock. The sample holder in the embodiment shown in Figure 1 is secured rigidly to the vessel head and has a continuous bore coaxial with the axis of rotation extending from the bottom of the holder to the vessel head. An entry hole in the head of the vessel forms a continuous passageway with bore. A control rod passes through this continuous passageway. The lower end of the control rod is rigidly attached to the support. The control rod is held in place longitudinally but allowed to rotate the supported plate about the axis of rotation relative to the sample holder. A seal is used to prevent loss of pressure between the control rod and the entry hole. The upper end of the control rod is attached to a support rotation controller. The rotation controller can be manually operated or, can be driven in an automated fashion by an electric motor driver attached to the upper end of said control rod. Ideally, the motor driver is controlled by a timer (not shown) without the need for human intervention during the entire experiment whereby individual samples are quenched at pre-selected and different times. As the support plate is rotated by the rotation controller, a support plate hole sequentially aligns with each of the holder chambers. The support plate hole is sized to allow individual samples placed within the holder chambers to drop into the quench zone when the hole and the relevant chamber are aligned. The control rod as shown in Figures 1, 2A, and 2B is custom fabricated to the desired specifications from 316L grade stainless steel bar stock. The sample chambers are open slots on the outer cylindrical surface of the holder. The sample retaining support is a circular plate mounted in a fixed position and shaped to fit closely to the outer diameter of the sample holder. The support in this embodiment has a slotted hole which sequentially aligns with the slots in the holder as the holder is rotated about its vertical axis of rotation, thus allowing individual samples to drop into the quench zone. The sample holder will have about 10 openings suitable for holding samples, arranged in a circle pattern. When the opening is not aligned with an individual chamber, the support will prevent a sample contained in that chamber from dropping into the quench zone. The relative motion of the holder and the support causes the opening to align with each of the chambers at some point in the movement and that alignment of the opening with the chamber will allow the sample in that chamber to drop to the quench zone. Figure 2A is an enlarged perspective view of the combined assembly of the sample holder, heater, insulation, support, control rod and bearing assembly shown in Figure 1.

The temperature of samples placed in the chambers in the sample holder is maintained by a coiled cable heater wound around the outside surface of the holder. Sample temperature can be controlled by installation of sample-monitoring thermocouples within one of the sample chambers. Electric lead and sheathed thermocouples through the vessel wall were used, respectively, to power the heater and monitor the temperatures of the samples from the exterior of the vessel. Such means must be capable of maintaining the pressure integrity of vessel. Control of the quench zone temperature is maintained by any known cooling means.

5. Testing of the technique

The apparatus has been actually built and tested in order to evaluate the feasibility of the conceptual design. Several important observations and improvements have been done:

In the embodiment shown in Figure 1, placement of a bearing assembly between support and sample holder is necessary in order to provide free rotation of the control rod when the reactor is operated under pressures. The bearing assembly can be constructed of metal, ceramic, or any material or combination of materials suitable for withstanding the stress and temperature required for maximum operating design conditions for the pressure vessel. The bearings used here are Grade C25 ceramic (alumina) balls, 0.125 inches (3.2 mm) in diameter, available from Hoover Precision Products, Sault Ste. Marie, Michigan.

The preliminary testing using Argon gas as pressure medium reveals that the gas serves as a strong heat sink that the heating of the furnace required much higher electric power than anticipated. Although any medium that does not hinder operation of the furnace can be used for pressuring the vessel cavity (cavity 2 in Figure 1), Helium gas was found so far particularly preferable due to its reduced load on the heater as compared to other typical mediums such as argon gas. Helium gas, which is easier to leak than Argon may limit the maximum pressure. The problem of the heating load become more severe with increasing pressures; it is no longer a problem at atmosphere pressure. The reduction of the gas volume by insert pyrophyllite block may also reduce heating load caused by the inert gas pressure medium. Each of these features contributes to the ability of the apparatus to achieve increased controlled heating rates and maximum temperature. Preferably, the apparatus has the capability of heating samples at rates up to 25 °C per minute at temperature up to 600 °C, and pressures up to 300 bars. The capability can be improved by using a high strength pressure vessel and by the reduction of heating load using a new pressure medium.

Minimizing free space between the samples and the sides of the chambers allows the sample to be maintained at a more uniform temperature along its length. In a particularly preferred embodiment, the homogeneity of the sample temperature is maximized by enclosing the sample capsule in a brass enclosure and capping the enclosure with a glass insulating plug, as illustrated in Figure 2B. The sample capsule can be fabricated from noble metals (e.g. gold) suitable to withstand the conditions of the experiment, without contaminating the enclosed sample.

The preliminary testing show that significant temperature may rise in the quench zone if no external cooling provided for the vessel. Means of cooling provided in the embodiment shown in Figure 1 by immersing the lower portion of the vessel in a water bath. Suitable thermocouples include but are not limited to sheathed thermocouples identified above. For certain applications of the apparatus where fast cooling of the samples (quench rates) are required, the quench zone temperature is preferably monitored by a quench-zone thermocouple, thus allowing feedback for control of the water bath temperature. However, the rate of heat removal from the samples is increased by reducing the temperature of the quench zone. The temperature of quench zone, therefore, depends on the desired heating and quenching rates required for each type of experiments.

6. Conclusion

The newly designed hydrothermal apparatus can significantly improve the efficiency of conventional techniques. The merits of this apparatus includes: (1)

multi-sample capability which allows rapidly quenching each individual sample sequentially along heating profile and significantly reduce the time and cost of experiments, (2) internally heated capability which enables samples heating at programmed heating rates. The apparatus, although capable to study most reaction kinetics for oil and gas generation and cracking, is limited by low temperatures and pressures capabilities compared to conventional techniques. The results of this preliminary testing suggest that the new technique so far may be conducted with more than ten samples at heating rates less than 30 °C/min. up to 600 °C with pressure up to 300 bars. The capability can be improved by further testing, especially in a high strength vessel and in new gas pressure media. This technique is particularly useful for the study of reactions the kinetics of organic and mineral reactions.

Acknowledgments

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出席第20屆國際有機地球化學會議報告

黃武良

參加會議過程

第20屆國際有機化學會議由歐洲有機地球化學協會主辦，2001年9月在法國Nancy舉行，全世界二十幾國學者專家與會，共發表論文350篇。本人受邀與會發表論文，論文題目為「MULTI-SAMPLE, PROGRAMMED-HEATING, AND RAPID-QUENCH APPARATUS FOR CONFINED OR MSSV PYROLYSIS。專題研討會議主題包括石油地球化學、環境地球化學、生物地球化學等。共分成8個sessions，其中本人參與的包括：(1) Oil / gas / reservoirs / migration，(2) Molecular and isotopic source indicators，(3) Environmental organic geochemistry， (4) Analytic developments in organic geochemistry。

與會心得

(一) Oil / Gas / Reservoirs / Migration

本 session 為本次會議的主軸，過去多年來有機地球化學很成功地應用在石油系統上，本會議在此方面的研究成果包括石油及源岩的的成熟度測定 (P/TUE1/01, Stojanovic, K., et al.)、石油的移棲(P/TUE1/49, Volk, H., et al.; P/TUE1/41,de Barros Penteado, H. L., et al.)、油氣的評估等(P/TUE1/20, Goncalves, , G.T.T., et al.)。有機地球化學的研究，趨向於使用高精密度的儀器，例如 GC-MS-MS 及 IRGCMS，此等儀器資料對於石油生成的機制及油-源岩和油-油對比，及石油的定年有創新性的貢獻。國內在此方面的研究以中油探採研究中心為主，學術界在此方面的研究甚少，未來油氣探勘上的研究應可往此方向發展。

(二) Molecular and isotopic source indicators

本 session 主要探討有機物分子及同位素應用在沉積物中有機物的來源上。生物指標及個別分子同位素的研究已從油氣探勘上的應用發展到海洋沉積環境及全球變遷的研究上。使用精密的儀器分析，追蹤有機沉積物的來源，在本討論會議中廣泛地被討論，許多新的資料(P/WED1/02, Ogihara, S. & Ashi, J.; P/WED1/18, Rutters, H.)顯示微生物中的生物指標，可提供海洋有積物來源的重要依據。

(三) Environmental organic geochemistry

本 session 主要探討油氣對於環境的污染(P/THU1/01, Kamp, H., et al.)及可能的整治方法(P/THU1/03, Mamajanov, I., et al.)。以微生物方法處理污染(P/THU1/19, de Oteyza, T. G., et al.; P/THU1/03, Mamajanov, I., et al.)，已經獲得相當進展。其中許多論文進行研究在自然界中，地質作用過程中生物對油氣的退化作用(biodegradation)，此等研究對於污染處理上提供重要的依據，國內地質科學界在此方面的研究甚少。未來地質界同環境工程界一起合作，往此方面發展是相當好的研究方向。

(四) Analytic developments in organic geochemistry

有機地球化學的發展十分依賴新的分析儀器的開發。本 session 中新的或改良的儀器，在會議中受到重視，其中鐳射激發螢光的顯微鏡(P/WED2/01, Xianming, X., et al.)，使得有機岩理學的研究，可能有新的發展。此外以紅外線光譜顯微探針研究礦物中石油的包裹體，對於研究石油的移棲相當有用。

建議

有機地球化學及微生物地球化學為近年來新興的地球科學學門之一。此等學門在油氣探勘與生產以及環境污染的應用上，有實質的價值。近年來國際上在此方面的研究及應用十分熱烈，國內在此方面的研究幾乎尚未開始。鑑於新興的學門，要迎頭趕上國際水準較容易，加上生物科技乃為國內未來發展的重點，以及石油探勘上的應用，因此建議國內地球科學界同化學及生物界進行跨領域的整合型計劃，此等研究結果不但具有極大之學術價值，並且可能在環保及能源應用上有實際的收穫。

攜回資料

本會議出版會議論文摘要集，內容包括所有與會所有論文的摘要。有興趣同仁可向本人借閱(wlhuang@ccms.ntu.edu.tw)。

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Abstracts Volume 2

G2R
Géologie et Gestion des Ressources minérales et énergétiques

European Association of Organic Geochemists

A MULTI-SAMPLE, PROGRAMMED-HEATING, AND RAPID-QUENCH APPARATUS FOR CONFINED OR MSSV PYROLYSIS

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Confined pressure pyrolysis using gold capsules as sample containers has been increasingly applied to the study of organic reactions, and oil/gas generation kinetics/yields (e.g. Landais et al., 1994; Behar, et al., 1997; Freund et al., 1993). The conventional apparatus such as the externally heated cold-seal pressure vessel, was restricted by its inefficiency, and limited to isothermal experiments. A new pyrolysis reactor (Huang and Otten, 2000) has been developed to improve the efficiency by simultaneously heating multiple reactant samples at programmed heating rates under pressure, and allowing individual samples to quench automatically at desired times along the heating profile without interrupting the experiments. Typically, the apparatus includes a pressure vessel (e.g. Parr type) having both a hot-zone and a quench-zone inside the vessel. The hot-zone is composed of a coil resistant-heater and a sample holder capable of holding ten or more sample capsules is mounted within the hot zone. Each individual capsule can be rapidly cooled at a desired run time while the others continue running under the pressure and temperature; it is equipped with means for selectively dropping individual capsules from the holder to the quench-zone at a time or times determined by the operator. A simplified version of the apparatus, which was modified to operate at one atmosphere pressure, may be used to effectively perform micro-scale seal tube (MSSV) experiments (Horsfield, et al., 1989).

The apparatus has actually been built and tested. Several lessons from experience gained from the apparatus include: (1) Placement of a bearing assembly between support and sample holder in order to provide free rotation of the control rod when the reactor is operated under pressure. (2) Use of Helium instead of Argon gas as pressure medium to minimize the heat sink. (3) Minimization of free space of the pressure chamber to reduce the temperature gradient along sample length. (4) Immersing of the lower portion of the vessel in a water bath, if necessary, to increase the quenching efficiency. The pressure vessel can significantly improve the efficiency of conventional techniques for confined-pressure pyrolysis. The merits of this apparatus include: (1) multi-sample capability which allows rapidly quenching each individual sample sequentially along heating profile and significantly reduce the time and cost of experiments; the sample can be quenched automatically at desired run time; (2) internally heated capability, which enables samples heating at fast programmed heating rates and enables us to study reaction kinetics; and (3) that its simplified version is ideal for performing MSSV pyrolysis. The apparatus, however, is currently limited by low temperature (< 600°C) and pressure (< 300 bars) capabilities compared to conventional techniques. This technique is particularly useful for the study of kinetics of organic and mineral reactions.

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