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Kerogen Pyrolysis in the Presence and Absence of Water and Minerals. 1. Gas Components

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Pyrolysis experiments on kerogen (Estonian Kukersite) were conducted in a confined system (gold capsules) in the presence and absence of water and various minerals, i.e., kaolinite, montmorillonite, calcite, and dolomite, respectively, at a fixed pressure of 50 MPa and in the temperature range 240–400 °C. For the four experiments in the presence of minerals and a large amount of deionized water (OC/mineral/water 1:24:7–10), the ratios of isobutane/*n*-butane and isopentane/*n*-pentane generally increase with temperature and mineral acidity. As to the two experiments for kerogen alone and kerogen plus a small amount of water (OC/water 1:1.5), these two ratios are relatively high at low temperature (280–320 °C) and substantially low at high temperature (320–400 °C) in comparison with the experiments in the presence of minerals and a large amount of deionized water. The ratios of ethene/ethane and propene/propane generally decrease with increasing temperature. At the same temperature, these two ratios increase with an increasing amount of water and decrease with increasing mineral acidity. Pyrolysis experiments on this Kukersite kerogen with various OC/water ratios (0–15) further demonstrated that the ratios of ethene/ethane, propene/propane, isobutane/*n*-butane, and isopentane/*n*-pentane increased with increasing water/OC ratio. In addition, the amount of the gas hydrocarbons varied significantly with water/OC ratio, i.e., from 83.20 to 109.70 mg/g of OC at 350 °C and from 271.50 to 340.07 mg/g of OC at 450 °C, with the water/OC ratio increasing from 0 to 15. The amount of CO₂ produced also increases substantially and consistently with that of gas hydrocarbons with water/OC ratio. The amount of oxygen in the generated CO₂ exceeds the oxygen in the initial kerogen in the experiments with water/OC ratios of 10 and 14.5 at 450 °C, indicating that water derived hydrogen and oxygen have been incorporated into gas hydrocarbons and CO₂.

Introduction

Numerous studies have demonstrated that the pyrolysates (hydrocarbons, polar components, and water) released from kerogen react with each other, and with kerogen; therefore, the reaction medium is important for the kerogen pyrolyzing process.^{1–7} In the classical confined pyrolyzing system developed by Monthioux et al.,^{8,9} the pyrolysate components (hydrocarbons, polar components, and water) and kerogen in the compressed gold capsules are closely in contact with each other; the medium in this pyrolysis system is comparable to source rocks in a natural system. Similarly, in the classical hylous

pyrolysis system developed by Lewan and co-workers,^{10–14} the pyrolysate components and water (released and added) can be partly retained in the kerogen networks within rock chips, and therefore, the reaction medium is also comparable to that of source rocks in a natural system. The most important feature for both pyrolysis systems is that the compositions of the pyrolysate components correlate well to natural crude oils and extracted bitumens from source rocks in sedimentary basins.^{8–10,14} As water is ubiquitous in a sedimentary basin, Lewan¹⁴ particularly emphasized the importance of water in hydrocarbon generation and expulsions: (1) water promotes thermal cracking, which leads to hydrocarbon generation, and inhibits carbon–carbon bond cross-linking, which results in pyrobitumen formation, and (2) dissolved water in the bitumen network of a source rock is critical to the formation and expulsion of an immiscible saturate-enriched oil phase.

The role of minerals on the pyrolysis of kerogen has been discussed in detail in a series of studies.^{15–20} One of the main

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conclusions of these studies is that catalysis occurs under dry conditions in the presence of montmorillonite, but no such effect is evident under hydrous conditions.^{16–20} In these previous studies, the pyrolysis experiments were performed in sealed glass tubes with low pressures and very large reaction volumes relative to the amounts of reactants.^{15–20} The reaction medium of these pyrolysis experiments is strikingly different from that of natural source rocks.

Previous studies have indicated that organic matter in marine sediments is primarily associated with the mineral phase because it seems impossible to separate the two phases by physical means and there is a direct proportionality between organic matter concentration and sediment surface area.^{21–23} Therefore, kerogen, except for organic detritals, in source rocks could also be closely associated with the mineral phase. When kerogen is isolated from source rocks by dissolving minerals, the natural association between the two phases is also destroyed. Although the kerogen is mixed with mineral and water during laboratory experiments, both the kerogen and minerals are surrounded and separated by water and, therefore, these two phases are difficult to contact with each other.

The purpose of our study is to reevaluate the catalytic effects of carbonate and clay minerals, that is, calcite, dolomite, kaolinite, and montmorillonite, on hydrocarbon generation from kerogen during laboratory experiments in the presence of water using a confined pyrolysis system. Before pyrolysis experiments, efforts have been made to establish, to some extent, the association (adsorption) between the minerals and the isolated kerogen, so that the reaction medium in our experiments best matches that of a source rock in a sedimentary basin. In addition, in order to differentiate the effects of added minerals and water on the hydrocarbon generation, a series of pyrolysis experiments with various water/OC ratios in the absence of minerals were also performed in the same confined system.

The results of our studies are presented in three parts. In part I, we report the amounts and compositions of gaseous components produced during pyrolysis experiments.

Experimental Section

Mineral Catalysis. Kerogen Isolation. The kerogen used for mineral catalysis experiments was separated from the Estonian Ordovician immature oil shale (kukersite). This immature oil shale was at first ground into powder (about 200 mesh) and then Soxhlet extracted with a solvent mixture of dichloromethane/methanol (93:7 vol/vol) for 72 h to obtain the original extract. After extraction, the sample (about 120 g) was treated with HCl (6 N) to remove the carbonate minerals at 80 °C for 8 h. The sample was then washed using deionized water to a pH value of about 6 after removing the HCl solution, followed by further treatment with HF/HCl (1:1) to remove silicate minerals at 80 °C for 8 h. After cleaning, the sample was again treated with HCl to remove the remaining inorganic materials. The organic carbon content of the kerogen is 67.4%, measured using a Heraeus Elemental Analyzer (CHN-O-RAPID).

Kerogen–Mineral “Mud” Preparation. Four minerals were used in this study, that is, kaolinite, montmorillonite, calcite, and dolomite. The pH values for these four minerals measured in mud (mineral/deionized water 1:5 wt) at 25 °C are the following: kaolinite, 4.99; montmorillonite, 9.88; calcite, 9.11; and dolomite, 8.84. The kaolinite, calcite, and dolomite used in this study are of high purity. X-ray diffraction analysis cannot detect any other minerals in these samples. The montmorillonite (Ca/Na mixed) contains minor quartz, as detected by X-ray diffraction analysis, but the purity of the montmorillonite is higher than 90%. The organic carbon contents of all four mineral samples are below detection (<0.01%). Before being mixed with kerogen, these mineral samples were Soxhlet extracted with a solvent mixture of dichloromethane/methanol (93:7 vol/vol) for 72 h and then exposed to open air for 2 weeks to allow complete evaporation of the solvents. About 1.5 g of dry kukersite kerogen was mixed with about 24 g of one of the above four minerals to obtain four mixtures with a total organic carbon content (TOC) of about 4 wt %. Then, deionized water was added, little by little, to make a mudlike sample. The mud was ground for 4 h for two purposes: (1) homogenizing the mud and (2) grinding the mud sample (kerogen and mineral) to as fine as possible. All the four mud samples were at first dehydrated at 45 °C to remove most of the water and then placed in a closed container in the presence of silica-gel drier to further slowly remove the remaining water at room temperature for 1.5 months. During the long dehydration process, we expect that the association (adsorption) between kerogen and the minerals would be established.

Gold Capsules and Sample Loading. All pyrolysis experiments were conducted in flexible gold capsules (4 mm outside diameter, 0.25 mm wall thickness, and 4 or 6 cm length) contained within steel pressure vessels. The capsules were welded at one end before being loaded with samples. The shorter capsules (4 cm length) were used for loading kerogen only (about 60 mg) or kerogen (about 60 mg) plus the same amount of deionized water, while the longer ones (6 cm length) were used for loading kerogen plus mineral and deionized water (470.90–673.12 mg of solid and 200 mg of deionized water). Once loaded, the open end of each capsule was purged with argon before being squeezed in a vise to create an initial seal, which was subsequently welded in the presence of argon. During welding, the previously welded end was submerged in cold water to prevent heating of reactants.

Pyrolysis Apparatus. Our experimental system permits 10 pressure vessels to be placed in a single big furnace. A fan is installed at the bottom of the furnace to keep the vessels inside under the same temperature conditions during the experiment. The vessels were previously filled with water. Two capsules were placed into each vessel. The internal pressure of the vessels, which were connected to each other with pipelines, was adjusted to 50 MPa by pumping water into the vessels before heating. It maintained automatically by pumping water into or out of the vessels during pyrolysis experiments. The error of the pressure is $< \pm 0.1$ MPa. In this study, five series of pyrolysis experiments were conducted at 240, 280, 320, 360, and 400 °C, respectively. For each series of experiments, 12 capsules (240–360 °C) or 15 capsules (400 °C) loaded with six types of samples and duplicates were placed into six or eight pressure vessels. The vessels were heated to the desired temperature during a 2 h time period and then heated isothermally for 72 h. A thermocouple is placed in the furnace attaching one of these vessels. The error of the temperature is $< \pm 1$ °C. After heating, the vessels were quenched to room temperature in cold water within 10 min. During quenching, the pressure was held at 50 MPa to prevent the capsules from leaking. After cooling, the pressure inside the vessel was gradually reduced to the atmosphere pressure.

C₁–C₅ Hydrocarbon Analysis. The amounts and compositions of C₁–C₅ hydrocarbons were analyzed in a device demonstrated in Figure 1. Before a capsule was pierced, the whole device was evacuated by a vacuum pump to reach an internal pressure of less than 1×10^{-4} Pa. Then, valves A, C, F, and G were closed while valves B, D, and E were opened. Once the capsule was pierced,

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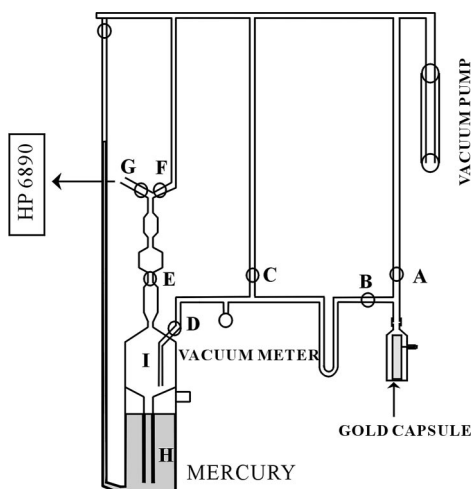


Figure 1. Schema of the device for the analysis of gaseous hydrocarbons from mineral catalysis experiments.

the gas filled the space entrapped by valves A, C, F, and G. After valve D was closed, the mercury was pushed from space H to space I up to valve E while the gas was compressed to the space among valves E, F, and G. Then, valve E was closed and the mercury was withdrawn from space I to space H. Valve D was opened again, and the remaining gas was absorbed from the tube and capsule spaces to space I. The volume of space I is 20 times more than that of the tube and capsule spaces. The push and withdrawal process was repeated several times until the internal pressure of the space entrapped by valves A, C, and D was less than 1×10^{-4} Pa, which indicated that the gas was completely compressed to the space among valves E, F, and G, in which the amount of gas was measured by the height of the mercury column when the top surface of mercury was pushed to reach valve E. When valve G was opened, the gas was automatically input to a HP6890 GC fitted with a 30 m \times 0.32 mm i.d. column coated with a 0.25 μ m film of CP-PARAPLOT-Q, employing nitrogen as the carrier gas. The oven temperature was programmed as follows: 40 $^{\circ}$ C for 2 min, raised from 40 to 180 $^{\circ}$ C at 20 $^{\circ}$ C/min, and then held at 180 $^{\circ}$ C for 5 min. As tested by external standard gas, this device has an accuracy of less than 0.5% in relative errors and is sensitive enough to collect and analyze the hydrocarbon gas lower than 0.01 mL.

Kerogen Pyrolysis with Various Water/OC Ratios. *Sample Preparation.* The aforementioned kukersite kerogen was used in this series of pyrolysis experiments. However, as this series of pyrolysis experiments were performed about 3 years later than the aforementioned mineral catalytic experiments, the kukersite kerogen was stored in a refrigerator during this period. The contents of organic carbon, hydrogen, oxygen, and nitrogen of this kerogen are 67.02, 8.26, 14.90, and 3.00%, respectively, measured just before the pyrolyzing experiment using an Elementar vario EL III. In comparison with the composition of kukersite kerogen reported by Derenne et al., that is, 67.0% C, 8.3% H, 12.8% O, 2.2% N, and 3.5% S,²⁴ the oxygen content of our kerogen sample is relatively high, possibly due to partial oxidation during storage.²⁵

Experimental Apparatus and Pyrolysis Processes. The pyrolysis experimental apparatus and processes are similar to those of the aforementioned mineral catalysis experiments. All pyrolysis experiments were conducted isothermally at 350 and 450 $^{\circ}$ C and a fixed pressure of 50 MPa for 72 h in flexible gold capsules (4 mm outside diameter, 0.25 mm wall thickness, and 60 mm length) contained within steel pressure vessels. About 30 and 10 mg of kerogen was used for the experiments at 350 and 450 $^{\circ}$ C, respectively, without or with the addition of deionized water in the amounts of 1, 3, 7, and 10 times of the kerogen, making up five types of samples in

total. For each type of sample at each run, one or two duplicate gold capsules were prepared.

Volatile Component Analysis. After pyrolyzing, for each sample type, one capsule was used for the analyses of volatile products. The analytical method is somewhat different from that of the aforementioned mineral catalysis experiments. The volatile components in the capsules were collected and concentrated in a device connected with an Agilent 6890N GC modified by Wasson/ECE Instrumentation (Figure 2). Initially, valve D was closed while valves A, B, and C were open. The whole device was evacuated by a vacuum pump to reach an internal pressure of less than 1×10^{-2} Pa. Valves A, B, and C were closed, and valve D was open to allow the standard gases to get into the space entrapped within valves A, B, and D, with a volume of 30.6 mL. Once valve D was closed, the amount of the standard gases could be determined by the pressure gauge. Valve B was open to allow gases to get into the 6890N GC, through which the GC analyses of both the organic and inorganic gas components were performed in an automatically controlled procedure. This modified GC is equipped with seven valves, eight columns, and three detectors, that is, a flame ionization detector (FID) for analyzing gas hydrocarbons (helium as a carrier gas), a thermal conductivity detector (TCD) for analyzing H_2 (nitrogen as a carrier gas), and another TCD for analyzing the other inorganic gases (helium as a carrier gas). The oven temperature for the hydrocarbon gas analysis was initially held at 70 $^{\circ}$ C for 6 min, ramped from 70 to 130 at 15 $^{\circ}$ C/min, from 130 to 180 at 25 $^{\circ}$ C/min, and then held at 180 $^{\circ}$ C for 4 min, whereas it was held at 90 $^{\circ}$ C for the inorganic gas analysis. The analysis of all gases was carried out by one single injection. An equation between the amounts and the values of FID and TCD responses for the gas components was obtained through a series of analyses of the standard gases with known amounts. The process for the sample analysis was generally similar to that of standard gas analysis. After the entire device was evacuated, all four valves were closed, and the gold capsule was pierced. Gas components filled the space entrapped within valves A, B, and D. Valve B was open to allow the components to be analyzed by the modified GC. The amounts of the gas components were determined from the values of FID and TCD responses and the aforementioned equation. As the total volume of gold, water, and kerogen of a capsule ranged from 0.10 to 0.40 mL, about 0.3–1.3% of the volume of the effective space entrapped within valves A, B, and D (30.6 mL), the corrected amounts of the gas components within the capsule were about 0.3–1.3% lower than those calculated from the equation. A test with external standard gases indicated that this device had an accuracy of less than 0.5% in relative errors.

Results

Mineral Catalysis Experiments. The amounts of C_1 – C_5 hydrocarbons for mineral catalysis experiments are shown in Table 1 and Figures 3 and 4. Gas geochemical parameters are shown in Table 1 and Figure 5. Amounts of ΣC_{1-5} hydrocarbons produced during pyrolysis experiments increased consistently from the range of 1.18–5.20 to 258.09–445.66 mg/g of OC with the temperature increasing from 280 to 400 $^{\circ}$ C (Table 1 and Figure 3). The ratio of $C_1/\Sigma C_{1-4}$ is the highest at 280 $^{\circ}$ C, ranging from 24 to 38 wt % (Table 1 and Figure 5a), but decreases dramatically at 320 $^{\circ}$ C, ranging from 16 to 24 wt %. For the experiment using montmorillonite, the ratio decreases further at 360 $^{\circ}$ C and then increases at 400 $^{\circ}$ C, while, for the other five experiments, it increases at both 360 and 400 $^{\circ}$ C. At 360 and 400 $^{\circ}$ C, this ratio is very similar among the six experiments, ranging from 19 to 24% and 22 to 25%, respectively.

The ratios of iC_4/nC_4 and iC_5/nC_5 for the four experiments using minerals increase with temperature, while the relations between the ratios and the temperature are much more complex for kerogen alone and in the presence of deionized water only (Table 1, Figure 5b and c).

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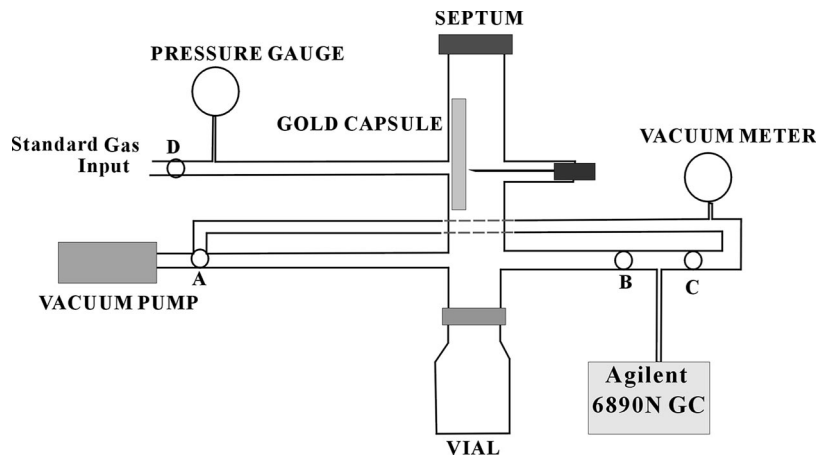


Figure 2. Schema of the device for the analysis of gaseous components from the pyrolysis experiments with various water/OC ratios.

Table 1. Amounts (mg/g of OC) of C₁–C₅ Hydrocarbons Produced during Pyrolysis Experiments^a

	ASS (mg)	OC (mg)	C ₁	C ₂ H ₄ (10 ⁻³)	C ₂ H ₆	C ₃ H ₆ (10 ⁻³)	C ₃ H ₈	iC ₄	nC ₄	iC ₅	nC ₅	ΣC ₁₋₅	AΣC ₁₋₅ (mg)	C ₁ / ΣC ₁₋₄ (wt)	C ₁ / ΣC ₁₋₄ (vol)	iC ₄ / nC ₄	iC ₅ / nC ₅	C ₂ H ₄ / C ₂ H ₆ (10 ⁻³)	C ₃ H ₆ / C ₃ H ₈ (10 ⁻³)
280 °C																			
Ker-3	67.33	45.83	0.52	0.58	0.66	2.50	0.65	0.086	0.258	0.059	0.126	2.37	0.109	0.24	0.44	0.33	0.47	0.89	3.86
Kw-15	60.63	40.86	0.58	0.52	0.72	3.16	0.67	0.100	0.286	0.099	0.147	2.62	0.107	0.25	0.44	0.35	0.67	0.73	4.72
Kao-3	592.10	24.04	1.30	9.39	1.40	19.48	1.12	0.314	0.562	0.172	0.273	5.20	0.125	0.27	0.48	0.56	0.63	6.68	17.33
Mon-3	470.90	19.97	0.84	9.58	0.72	40.86	0.45	0.016	0.180	0.007	0.075	2.35	0.047	0.37	0.59	0.09	0.09	13.37	89.85
Cal-3	628.86	26.60	1.08	13.42	1.16	90.20	0.97	0.021	0.491	0.013	0.270	4.14	0.110	0.28	0.50	0.04	0.05	11.59	92.78
Dol-4	613.54	25.43	0.43	7.02	0.35	23.62	0.22	0.007	0.096	0.003	0.039	1.18	0.030	0.38	0.59	0.07	0.08	19.93	106.2
320 °C																			
Ker-6	61.14	41.21	4.10	BD	7.03	5.07	7.96	0.76	5.48	1.07	4.25	31.07	1.280	0.16	0.33	0.14	0.25	0	0.65
Kw-17	60.31	40.65	5.88	BD	8.95	12.47	8.89	2.21	4.94	1.99	2.89	36.06	1.466	0.19	0.38	0.45	0.69	0	1.40
Kao-5	673.12	27.32	5.16	7.23	7.72	34.35	8.44	3.99	5.12	2.89	2.23	35.80	0.978	0.17	0.35	0.78	1.30	0.94	4.07
Mon-7	536.87	22.76	2.65	7.77	3.18	69.47	2.95	0.25	1.81	0.45	1.03	12.50	0.285	0.24	0.45	0.14	0.44	2.44	23.56
Cal-5	568.74	24.06	5.09	17.79	7.01	189.25	7.79	0.71	6.13	1.33	4.20	32.88	0.791	0.19	0.38	0.12	0.32	2.54	24.31
Dol-6	613.44	25.43	3.98	10.87	5.40	133.45	5.94	0.45	5.29	0.72	3.21	25.46	0.647	0.19	0.38	0.08	0.22	2.01	22.46
360 °C																			
Ker-8	60.34	40.67	22.13	BD	28.21	9.84	32.23	2.88	23.34	4.75	17.25	132.53	5.390	0.20	0.40	0.12	0.28	0	0.31
Kw-19	61.00	41.11	22.77	BD	28.54	24.73	34.74	4.82	23.65	8.03	15.33	139.42	5.732	0.20	0.39	0.20	0.52	0	0.71
Kao-8	616.19	25.01	27.62	10.39	31.64	47.50	40.65	25.68	22.84	25.78	12.98	188.54	4.715	0.19	0.39	1.12	1.99	0.33	1.17
Mon-8	485.12	20.56	26.59	33.13	29.87	439.93	36.55	12.54	23.56	13.32	12.70	156.88	3.225	0.21	0.41	0.53	1.05	1.11	12.04
Cal-7	614.23	25.98	26.84	23.37	31.79	458.97	40.61	9.16	25.00	4.23	4.84	143.43	3.726	0.20	0.40	0.37	0.87	0.74	11.30
Dol-8	623.97	25.86	22.80	19.12	27.56	458.74	34.06	4.82	23.57	4.44	11.34	130.20	3.367	0.20	0.40	0.20	0.39	0.69	13.47
400 °C																			
Ker-11	56.25	37.91	58.02	BD	62.31	38.92	70.79	12.17	44.81	13.68	26.39	290.86	11.027	0.23	0.44	0.27	0.52	0	0.55
Kw-23	59.87	40.35	57.46	BD	61.72	50.65	70.81	14.43	33.65	9.88	9.17	258.09	10.414	0.24	0.45	0.43	1.08	0	0.72
Kao-12	585.73	23.79	82.40	BD	65.83	18.57	89.09	48.06	38.63	29.82	13.00	368.15	8.758	0.25	0.48	1.24	2.29	0	0.21
Mon-12	486.38	20.62	94.55	33.83	85.42	236.74	105.15	47.93	56.70	31.29	22.14	445.66	9.189	0.24	0.46	0.85	1.41	0.40	2.25
Cal-12	615.72	26.06	75.22	37.42	77.16	334.21	101.59	29.60	61.85	22.54	28.32	399.48	10.410	0.22	0.43	0.48	0.80	0.49	3.29
Dol-12	655.24	27.16	74.48	47.12	76.88	570.03	94.89	16.39	56.14	13.76	23.37	358.86	9.747	0.23	0.44	0.29	0.59	0.61	6.01

^a ASS, amount of solid sample (mg); OC, amount of total organic carbon (mg); AΣC₁₋₅ (wt), amount of C₁–C₅ hydrocarbons (mg) produced in each capsule; Ker-, kerogen alone; Kw-, kerogen plus deionized water (OC/water = 1:1.5 wt); Kao-, kerogen plus kaolinite and deionized water (OC/kaolinite/water = 1:24:7–10 wt); Mon-, kerogen plus montmorillonite and deionized water (OC/montmorillonite/water = 1:24:7–10 wt); Cal-, kerogen plus calcite and deionized water (OC/calcite/water = 1:24:7–10 wt); Dol-, kerogen plus dolomite and deionized water (OC/dolomite/water = 1:24:7–10 wt).

The ratios of iC_4/nC_4 and iC_5/nC_5 for the experiment using kaolinite increase consistently with temperature and are significantly higher than those for all of the other experiments. These ratios for the experiment using montmorillonite are relatively low at low temperatures (280–320 °C), but they increase rapidly, only next to those of the experiment using kaolinite at high temperatures (360–400 °C). As to the experiments for kerogen alone and using deionized water only, these two ratios are relatively higher than those in the other experiments except that using kaolinite at low temperature (280–320 °C) but relatively lower at higher temperature (360–400 °C). For the experiments using calcite and dolomite, respectively, these two ratios remain relatively lower in the whole temperature range (280–400 °C).

Only trace amounts of ethene and propene were produced during mineral catalysis experiments (Table 1, Figure 5d and e). On the basis of the ethene/ethane and propene/propane ratios, we can classify the six experiments into three groups. In the first group, including the three experiments using montmorillonite, calcite, and dolomite, respectively, these two ratios are the highest. In the second group, including the only experiment using kaolinite, these two ratios are in between the first group and the last group except that they are lowest at 400 °C. In the last group, including the remaining two experiments with kerogen alone and using deionized water only, these two ratios are the lowest except at 400 °C. For all six experiments, ethene/ethane is lower than propene/propane, and both ratios decrease with temperature increasing except that the propene/propane

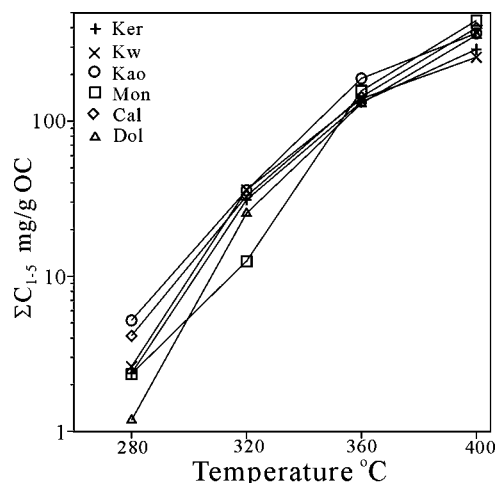


Figure 3. The total amounts of ΣC_1-C_5 hydrocarbons produced at 280–400 °C.

ratio for kerogen alone and using deionized water only increases slightly from 360 to 400 °C (Table 1, Figure 5d and e).

Pyrolysis Experiments with Various Water/OC Ratios.

The amount of gas hydrocarbons (ΣC_{1-5}) varies from 83.20 to 109.70 mg/g of OC at 350 °C and from 271.50 to 340.07 mg/g of OC at 450 °C (Table 2 and Figure 6a). The amount of CO_2 changes consistently with the amount of gas hydrocarbons and water/OC ratio increasing. It ranges from 81.88 to 137.70 mg/g of OC at 350 °C and 120.44 to 360.35 mg/g of OC at 450 °C (Table 2 and Figure 6b). Both the amounts of H_2 and H_2S produced increase with the amount of water increasing (Table 2 and Figure 7). However, the amount of H_2 increases consistently with the amount of added water increasing, while the amount of H_2S increases rapidly at a range of water/OC ratio of 0–4 and slowly at a water/OC ratio >4 . As H_2S can be dissolved in water considerably and the amount of H_2S dissolved in water was not measured in our experiment, the total amount of H_2S produced during pyrolysis experiments with water was higher than the measured value.

The ratio of $C_1/\Sigma C_{1-4}$ ranges from 18 to 20 wt % at 350 °C and 45 to 49 wt % at 450 °C (Table 2 and Figure 8). At 350 °C, the iC_4/nC_4 and iC_5/nC_5 ratios are relatively low and increase consistently with the amount of deionized water increasing. At 450 °C, the iC_4/nC_4 ratio is very high and increases dramatically with the amount of deionized water increasing while the iC_5/nC_5 ratio remains in a narrow range of 1.16–1.47 with and without the addition of deionized water (Table 2 and Figure 9a and b). Only trace amounts of ethene and propene were produced during the experiments (Table 2 and Figure 9c and d). Ethene/ethane and propene/propane ratios increase with the amount of deionized water increasing for the kerogen at 350 and 450 °C (Figure 9c and d).

Discussion

Ratios of iC_4/nC_4 and iC_5/nC_5 and Influencing Factors.

Previous pyrolysis studies have suggested that, in petroleum formation process, *n*-alkanes are formed by free radical reactions, whereas the branched isoalkanes arise from two processes: (1) free radical cracking of branched fragments and components of kerogen and bitumens and (2) carbonium ion reaction of α -olefins with protons which are promoted under acidic

conditions.^{26–28} As documented by previous pyrolysis and mild chemical degradation studies, the kukersite kerogen rarely bears branched fragments.²⁹ Therefore, the carbonium ion reaction is primarily responsible for the branched isoalkane formation in the pyrolysates of this kerogen.

As demonstrated in Table 1 and Figure 5b and c, the variation trends of the iC_4/nC_4 and iC_5/nC_5 ratios among the four experiments in the presence of kaolinite, montmorillonite, calcite, and dolomite at 280 °C are consistent with the pH values of these four minerals measured at 25 °C. Because of the lowest pH value of kaolinite (4.99), the iC_4/nC_4 and iC_5/nC_5 ratios were substantially higher in the presence of kaolinite than those in the presence of other minerals. Although the pH value of montmorillonite is the highest among the four minerals measured at 25 °C in the presence of deionized water, the ratios of iC_4/nC_4 and iC_5/nC_5 are slightly higher at 280–320 °C and substantially higher at 360–400 °C in the presence of montmorillonite than those in the presence of calcite and dolomite, respectively. This result may be interpreted as that montmorillonite bears many acidic sites on its surfaces.^{30–33}

The ratios of iC_4/nC_4 and iC_5/nC_5 were generally low in the two experiments in the presence of calcite and dolomite, respectively (Table 1 and Figure 5b and c), which reflected the nonacidic (basic) nature of these two minerals.¹⁷ At 280 °C, the ratios of iC_4/nC_4 and iC_5/nC_5 were slightly lower in the presence of calcite than in the presence of dolomite, which was consistent with the pH values of these two minerals measured at 25 °C. However, it was opposite at 320 °C and higher temperature, which may indicate the changes of the pH values of these two experiments at high temperature.

Tannenbaum and Kaplan^{16,17} found that the iC_4/nC_4 ratio was significantly higher for kerogen in the presence of montmorillonite than for kerogen alone or in the presence of other minerals, that is, Illite, and calcite during anhydrous pyrolysis, and believed that this phenomenon is indicative of cracking via the carbonium ion mechanism which is induced by acidic sites of this clay during anhydrous pyrolysis. However, they also found that this ratio was similar among the above experiments, which indicated the absence of the catalytic effect of montmorillonite during hydrous pyrolysis. Tannenbaum and Kaplan^{16,17} performed their experiments using sealed glass tubes with low pressure and very large reaction volumes relative to the amounts of reactants. In their experimental system, montmorillonite efficiently adsorbed the kerogen and its pyrolysates onto the surfaces and exhibited a strong catalytic effect under anhydrous conditions, whereas it preferentially adsorbed water, rather than kerogen and its pyrolysates, and therefore demonstrated little catalytic effect under hydrous conditions. In contrast, our experiments were performed in a confined system with very low reaction volume relative to the amount of reactants. Although deionized water was added, minerals could be in contact with the kerogen and its pyrolysates due to the

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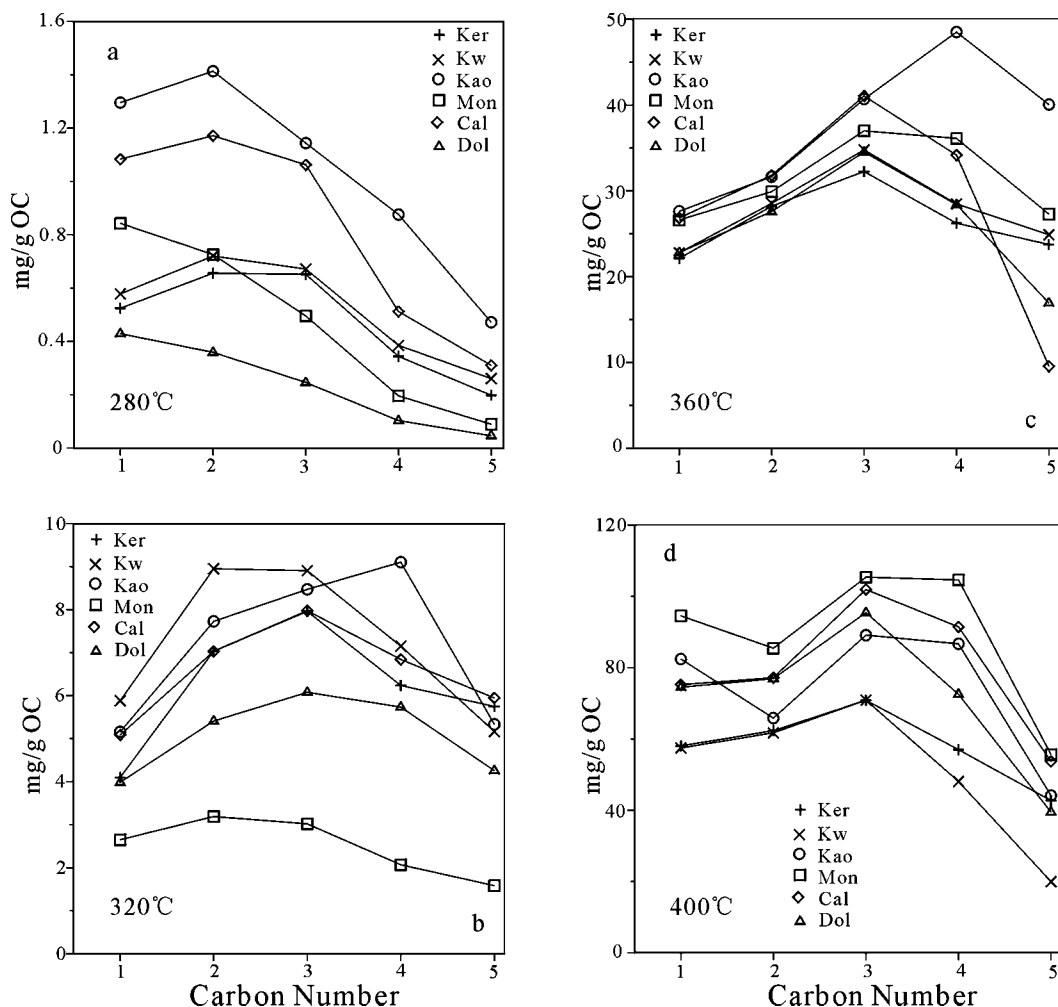


Figure 4. Quantities of C₁–C₅ hydrocarbons produced during kerogen pyrolysis: (a–d) the amounts of C₁–C₅ hydrocarbons produced at 280, 320, 360, and 400 °C, respectively. For Ker-, Kw-, Kao-, Mon-, Cal-, and Dol-, see Table 1.

establishment of the association (adsorption) between the minerals and the kerogen prior to pyrolysis experiments and low volume of the reaction cell during pyrolysis experiments.

The ratios of iC_4/nC_4 and iC_5/nC_5 for kerogen alone and in the presence of deionized water only are considerably higher than those in the presence of montmorillonite, calcite, dolomite, and sometimes kaolinite, respectively, at 280 °C (Figure 5b and c). This result suggests the strong acidic conditions for these two experiments, which may be accounted for by the generation of CO₂, H₂S, and organic acids, as demonstrated in many previous studies^{13,35,36} and in the pyrolysis experiments with various water/OC ratios in the present study (Table 2 and Figures 6 and 7). For the experiments in the presence of minerals, the pH value was buffered. The ratios of iC_4/nC_4 and iC_5/nC_5 were substantially low in the experiments for kerogen alone at 320 °C and higher temperatures, in comparison with those in the presence of minerals (Figure 5b and c). This result is inconsistent with the acidic catalysis effect, and will be further discussed later.

Hydrogenation of Gas Olefins. It has been suggested that anhydrous pyrolysis produces a large amount of olefins while

hydrous pyrolysis does not.¹⁰ However, Tannenbaum and Kaplan^{16,17} demonstrated that olefins were produced in the C₂–C₆ range in comparable amounts under both hydrous and anhydrous pyrolyses. Seewald et al.³⁷ provided another example which indicated that ethene and propene were produced in considerable amounts relative to ethane and propane during their pyrolysis experiment, in which a high water/rock mass ratio was employed to guarantee only aqueous phase and solid sample present in the reaction cell. Furthermore, Lewan¹⁴ demonstrated that gas olefins in C₂–C₄ range in trace amounts were produced in most of his pyrolysis experiments, under both hydrous and anhydrous conditions. In our experiments, the abundances of the produced olefins are very low (Tables 1 and 2, Figures 5d and e and 9c and d). For example, the ratios of ethene/ethane and propene/propane in our experiments are about 1 to 2 orders lower than those in the experiments performed by Tannenbaum and Kaplan^{16,17} and by Seewald et al.²² under similar temperature and heating time conditions.

Gas olefins are unstable and are readily hydrogenated into saturated hydrocarbons.^{16,17} Leif and Simoneit³⁸ found that a homologous series of terminal *n*-alkenes and *n*-alkanes were released after 1 h from the kerogen and present in a 1:2 ratio during hydrous pyrolysis on Messel shale, whereas these

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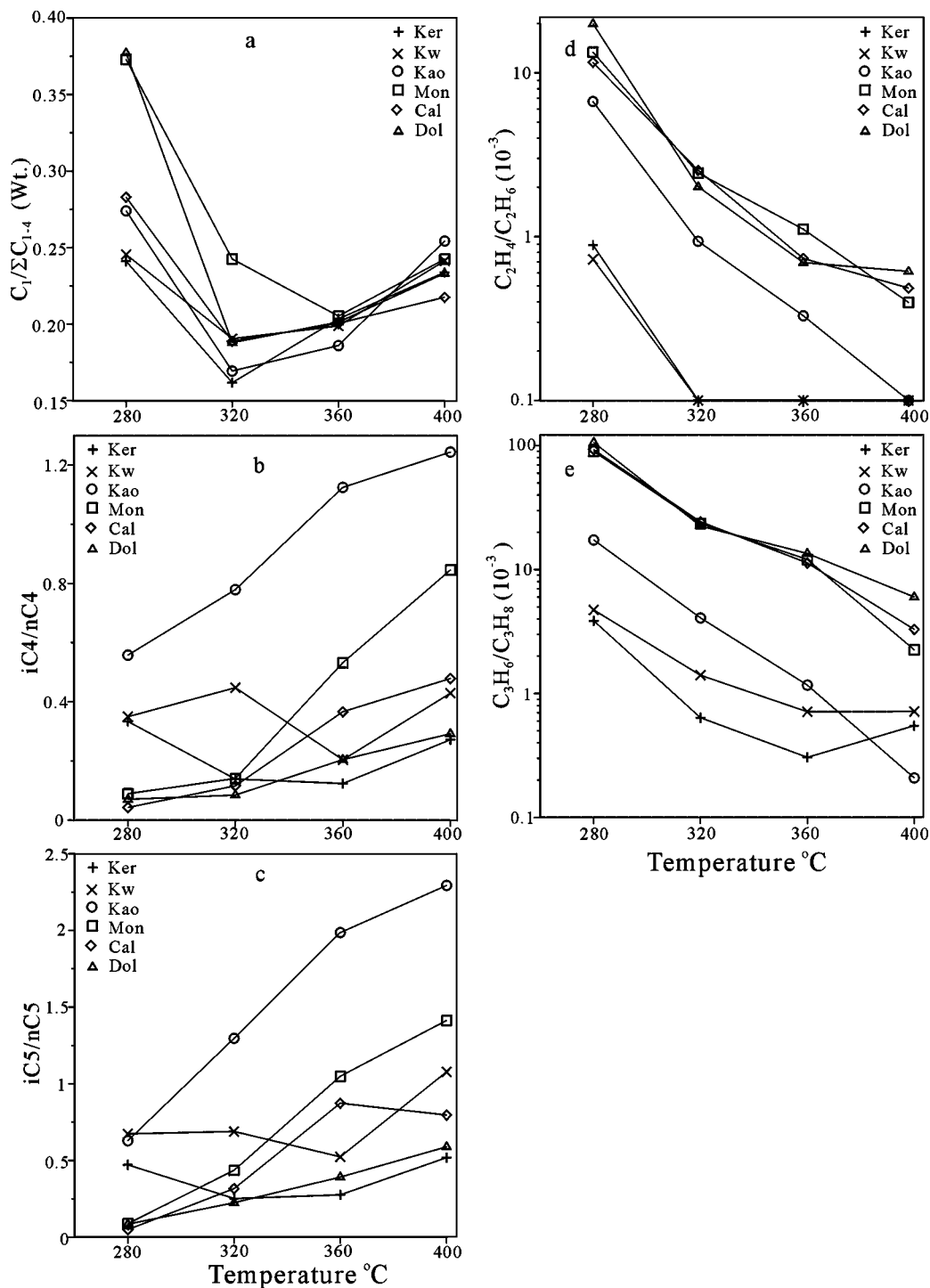


Figure 5. Selected gas hydrocarbon parameters vs temperatures. For Ker-, Kw-, Kao-, Mon-, Cal-, and Dol-, see Table 1.

terminal *n*-alkenes were not detected in either the 36 or 72 h runs but were likely present at a low, steady-state concentration. Leif and Simoneit³⁸ demonstrated that olefin model compounds, such as 1,13-tetradecadiene and 1-hexadecene, did not transform into the corresponding *n*-alkanes in pure water, whereas they were hydrogenated into the corresponding *n*-alkanes with the addition of Messel shale or elemental sulfur in hydrous pyrolysis experiments. They clearly revealed that, (1) in the presence of pure D₂O, deuterium did not incorporate in the alkane model compound but only incorporated in the alkene model compounds via acid-catalyzed isomerization of the double bond and, (2) with the addition of Messel shale or elemental sulfur, deuterium incorporated in the alkane via a free radical pathway and in the

alkenes via both the free radical and acid-catalyzed, ionic pathways. These results demonstrated that kerogen, bitumen, and minerals in the shale and elemental sulfur play the catalytic role in the alkene hydrogenation and hydrogen transfer from water to alkenes.³⁸

Smith et al.³⁹ carried out an interesting study on hydrous pyrolysis of model compounds which contain long chain *n*-alkyl constituents, that is, *n*-alcohol, di-*n*-ketone, di-*n*-ether, *n*-acid, and alkyl aromatics, and so forth. They indicated that the transformations of these model compounds into alkanes were

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Table 2. Amounts of Gas Hydrocarbons and Non-hydrocarbons (mg/g of OC) Produced in the Pyrolysis Experiments^a

	water/ OC	C ₁	C ₂ H ₄ (10 ⁻³)	C ₂ H ₆	C ₃ H ₆ (10 ⁻³)	C ₃ H ₈	iC ₄	nC ₄	iC ₅	nC ₅	CO ₂	H ₂	H ₂ S	ΣC ₁₋₅	C ₁ /ΣC ₁₋₄ (wt)	iC ₄ /nC ₄	iC ₅ /nC ₅	C ₂ H ₄ / C ₂ H ₆ (10 ⁻³)	C ₃ H ₆ / C ₃ H ₈ (10 ⁻³)
350 °C																			
K	0	12.29	1.01	15.91	8.63	19.31	1.86	16.61	2.95	14.15	81.88	0.051	11.86	83.09	0.19	0.11	0.21	0.064	0.447
Kw-1	1.40	14.43	3.95	17.63	45.89	21.10	4.65	14.89	5.90	9.85	120.68	0.111	19.66	88.51	0.20	0.31	0.60	0.224	2.175
Kw-2	4.07	16.24	9.03	19.05	107.00	22.99	8.37	15.11	8.30	9.04	136.97	0.171	25.99	99.21	0.20	0.55	0.92	0.474	4.655
Kw-3	9.02	15.65	16.38	17.98	188.38	21.15	10.38	13.63	9.17	8.18	137.70	0.279	26.79	96.35	0.20	0.76	1.12	0.911	8.908
Kw-4	13.80	15.84	23.49	17.53	274.02	22.19	14.55	15.47	13.73	10.06	136.88	0.424	29.03	109.67	0.18	0.94	1.36	1.34	12.347
450 °C																			
K	0	133.41	20.09	83.82	78.88	45.42	6.67	1.73	0.19	0.17	120.44	0.403	22.83	271.50	0.49	3.86	1.16	0.24	1.74
Kw-1	1.47	130.61	36.60	88.69	141.23	59.99	7.84	1.83	0.20	0.14	216.76	0.698	31.96	289.48	0.45	4.28	1.38	0.41	2.35
Kw-3	10.00	145.17	122.30	93.31	309.74	63.58	7.03	0.80	0.13	0.09	335.31	1.413	36.28	310.54	0.47	8.76	1.47	1.31	4.87
Kw-4	14.50	166.89	177.10	100.90	398.74	64.47	6.45	0.60	0.11	0.07	360.35	1.775	38.56	340.07	0.49	10.66	1.45	1.76	6.18

^a K, kerogen alone; Kw-1 to Kw-4, kerogen plus deionized water.

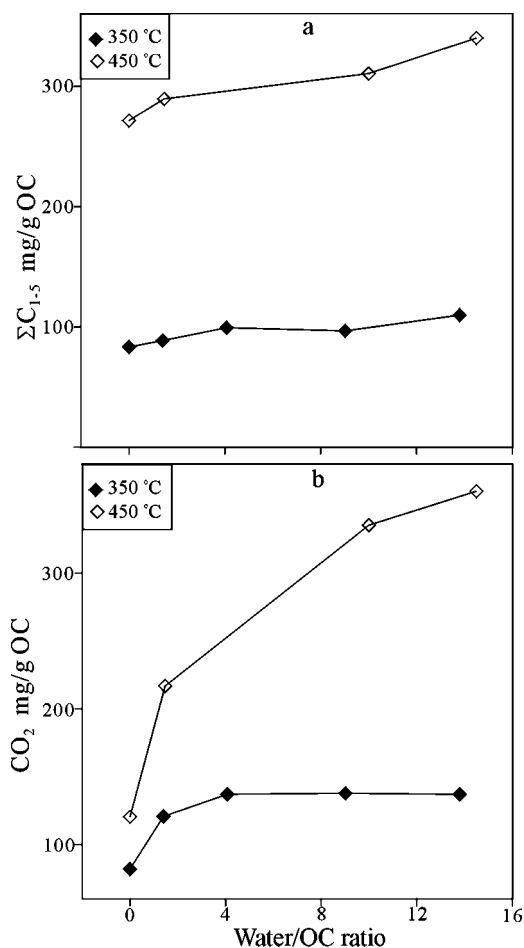


Figure 6. The amounts of gas hydrocarbons and CO₂ versus water/OC ratio.

promoted with the addition of brown coal, and the transformation rates increased with the ratios of the added coal to the model compounds.³⁹ The conversions of these components to *n*-alkanes were completed by a series of reactions, obviously including hydrogenation of *n*-alkenes. They concluded that the presence of carbonaceous material is essential for the generation of *n*-alkanes from the *n*-alkyl components and believed that the brown coal plays multiple roles for these conversions, a major one being the role of a hydrogen donor.³⁹ However, the transformation rate decreased unexpectedly when molecular hydrogen (H₂) was added in their experiments.³⁹ These results demonstrated during the hydrogenation *n*-alkenes did not react directly with molecular H₂ in hydrous pyrolysis experiments. Therefore, they³⁹ suggested that one role of the brown coal

appears to be as a source of exchangeable active hydrogen. Hesp and Rigby⁴⁰ and McMillen et al.⁴¹ reported a decrease of the alkane/alkene ratio when an excess amount of water was added in their experiments. Michels et al.³ suggested the following mechanisms for the incorporation of water derived hydrogen into hydrocarbons: (1) hydrogen exchange between water and an intermediate acidic species through the acid–base or oxidation–reduction mechanism; (2) transfer of a hydrogen radical from the intermediate compound to the organic radical by a radical mechanism. Mansuy et al.⁶ and Mansuy and Landdais⁷ have also demonstrated that water acts as an efficient hydrogenating agent only in the presence of polar components in the confined pyrolysis experiments on coal.

In the pyrolysis experiments with various water/OC ratios, the ratios of ethene/ethane and propene/propane increased with increasing water/OC ratio (Figure 9c and d). In the mineral catalysis experiments, these two ratios also increased in the order for kerogen alone < kerogen plus water (water/OC 1.5) < kerogen, water and mineral (water/OC 7–10) at temperatures lower than 400 °C (Figure 5d and e). Furthermore, the hopene/hopane ratios vary similarly as the ethane/ethane and propene/propane ratios, as documented in part 3.⁴² These results demonstrate that the hydrogenation rate of olefins decreased with increasing water/OC ratio, consistent with the aforementioned previous studies.^{38–41}

The hydrogenation rate of olefins substantially influenced the iso-alkane/*n*-alkane ratio: olefins released from kerogen and bitumen degradation are more likely hydrogenated into *n*-alkanes and less likely transformed into iso-alkanes when the hydrogenation rate of olefins is higher. As a result, the *i*C₄/nC₄ and *i*C₅/nC₅ ratios were low in the experiments for kerogen alone at 320 °C and higher temperatures, in comparison with those in the presence of minerals with a water/OC ratio of 7–10 (Figure 5b and c), and increased with increasing water/OC ratio (Figure 9a and b). In addition, the low ratios of ethene/ethane and propene/propane indicated the high hydrogenation rate of olefins in the experiment using kaolinite in comparison with those in the experiments using the other minerals (Figure 5d and e), which can be ascribed to the acidic catalysis, consistent with the previous studies.^{16,17,28,43}

Dryness Value C₁/ΣC₁₋₄. As demonstrated in Table 1 and Figure 5a, the ratio of C₁/ΣC₁₋₄ decreases from the highest at

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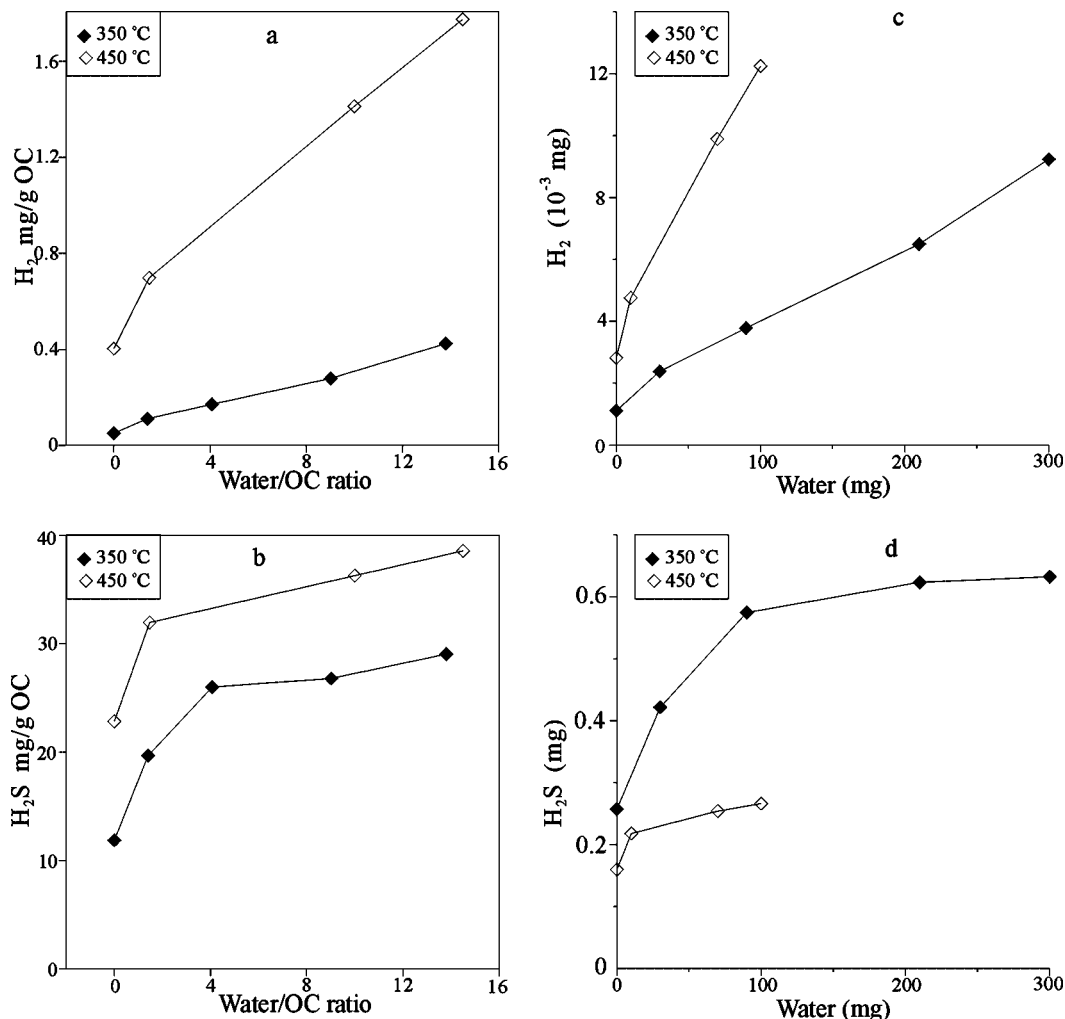


Figure 7. The amounts of H_2 and H_2S (mg/g of OC) versus water/OC ratio and the amounts of H_2 and H_2S (mg) versus the amount of water (mg).

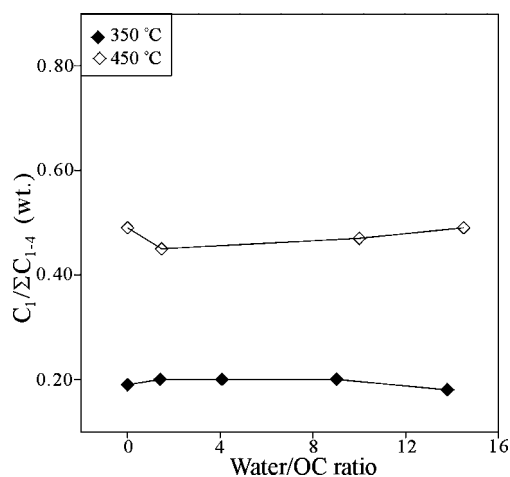


Figure 8. $C_1/\Sigma C_{1-4}$ ratio versus water/OC ratio.

280 °C to the lowest at 320–360 °C and then increases again at 360–400 °C. It could be expected to be even higher at 240 °C than at 280 °C. The variation trend of this ratio in our experiments is consistent with many previous studies.^{17,44} The mechanism behind this is unclear to us. It is interesting to note that this ratio is the lowest when the amount of produced bitumen is the highest at 320 °C except for the experiment using

montmorillonite (Figure 5a).⁴² This exception can be ascribed to the significantly lower amounts of produced bitumen and gaseous hydrocarbons in the experiment using montmorillonite than the other experiments at 320 °C.⁴² It can be expected that the ratio of $C_1/\Sigma C_{1-4}$ could decrease to the lowest level while the amount of produced bitumen could further increase to the highest level at a slightly higher temperature than 320 °C in the experiment using montmorillonite. This ratio steadily increases with temperature or maturation after the amount of the produced bitumen has reached the highest level. Whether and how this ratio is related to the generation and degradation of bitumen is unclear to us.

The $C_1/\Sigma C_{1-4}$ ratio is very similar among the six cases at a certain temperature in the range 320–400 °C (Figure 5a) except that it is relatively higher in the experiment using montmorillonite at 320 °C, as discussed above. This result indicates that neither mineral acidity nor the amount of water influenced the $C_1/\Sigma C_{1-4}$ ratio considerably in our experiments after the amount of produced bitumen reached the highest level.

As introduced by Mongo,^{45–47} the ratio of $C_1/\Sigma C_{1-4}$ for natural gas is averaged at about 85 wt %. This ratio is substantially low in our experiments, especially at 320–400 °C (Table 1 and Figure 5a), in comparison with the data of natural gas. However, as documented by Mongo,^{45–47} it is a common phenomenon that

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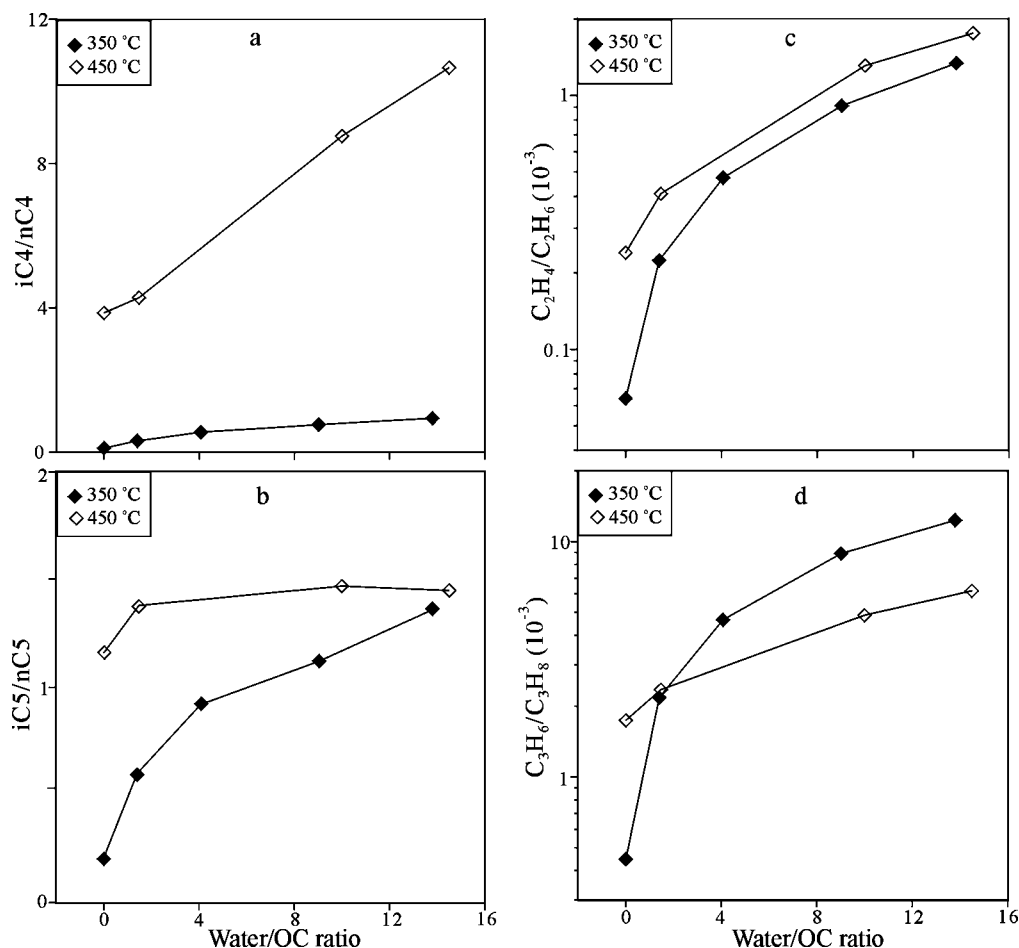


Figure 9. Ratios of iC_4/nC_4 , iC_5/nC_5 , C_2H_4/C_2H_6 , and C_3H_6/C_3H_8 versus water/OC ratio.

the gaseous hydrocarbons produced from experimental pyrolysis are relatively poorer in methane than is natural gas. In the study by Lewan,¹⁴ this ratio for Woodford Shale and its kerogen under various conditions ranges from 40.4 to 51.5 mol % at about 330 °C (70–72 h) and from 50.1 to 66.6 mol % at 350 °C (72 h).

Mongo^{45–47} ascribed the high abundance of methane relative to C_2 – C_4 hydrocarbons to transition metal catalysis in a natural environment in comparison with the pyrolysis experiments. As demonstrated in our experiments and many previous experimental studies, the $C_1/\Sigma C_{1-4}$ ratio decreased with increasing experimental temperature at <320 °C.^{17,37,44} The high $C_1/\Sigma C_{1-4}$ ratio for gas hydrocarbons in a natural environment may be ascribed to the low temperature (<200 °C) at which gas hydrocarbons are generated in sedimentary basins in comparison with pyrolysis experiments. The transition metal catalysis may not be essentially needed for natural gas generation in sedimentary basins.

Incorporation of Water Derived Hydrogen and Oxygen in Gas Hydrocarbons and Carbon Dioxide. Numerous studies have documented the incorporation of water derived hydrogen into hydrocarbon generation during kerogen or source rock pyrolysis experiment.^{12,14,37,48,49} In addition, some previous studies demonstrated that the amount of water released from kerogen was the lowest while the amount of C_7 – C_{14} hydrocarbons reached the highest at 325–400 °C in pyrolyzing experiments in a confined system without the addition of water,

Table 3. Oxygen Mass Balance (mg/g of OC) for the Pyrolysis Experiments^a

	water/OC	CO ₂	O
350 °C			
K	0	81.88	59.55
Kw-1	1.40	120.68	87.77
Kw-2	4.07	136.97	99.61
Kw-3	9.02	137.70	100.15
Kw-4	13.80	136.88	99.55
450 °C			
K	0	120.44	87.59
Kw-1	1.47	216.76	157.64
Kw-3	10.00	335.31	243.86
Kw-4	14.50	360.35	262.07

^a K, kerogen alone; Kw-1 to Kw-4, kerogen plus deionized water; O, the amount of oxygen in the measured CO₂. The amount of oxygen in the initial kerogen was 222.32 mg/g of OC.

implying that water was consumed during the peak stage of hydrocarbon generation.^{4,50} The result that the amounts of both gas hydrocarbons and CO₂ increased with increasing water/OC ratio at 350 and 450 °C in our experiments may indicate that water derived hydrogen and oxygen were incorporated in gas hydrocarbons and carbon dioxide and the incorporation extent increased with increasing water/OC ratio (Table 2, Figure 6). In particular, the amount of oxygen in the generated CO₂ exceeds the oxygen of the initial kerogen in the experiments with water/OC ratios of 10 and 14.5 at 450 °C (Table 3). An alternative interpretation to the amounts of gas hydrocarbons and CO₂ increasing with water/OC ratio is related to the oxygen

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in the kerogen that may be released in different forms. It may be preferentially released as H₂O in the experiments without the addition of water or with low water/OC ratio or as CO₂ in the experiments with high water/OC ratio. Lorient and Behar⁵¹ have suggested that oxygen in kerogen would be released in different forms under different pyrolysis systems, that is, preferentially in the form of CO₂ in closed systems and in the form of H₂O in open systems. For both causes (water incorporation and oxygen releasing in different forms), the overall results are similar.

Lewan¹⁴ found that the amounts of gas hydrocarbons and molecular hydrogen (H₂) are relatively higher while the amount of oil components is substantially lower under anhydrous conditions relative to hydrous conditions at 300–350 °C, which is somewhat different from our result. This inconsistency can be mainly attributed to the different experimental conditions. Lewan¹⁴ used stainless-steel vessels as the reaction cells, whose volumes remained unchanged and were occupied by a helium and solid phase during the pyrolysis experiments in the absence of water. Therefore, this experimental condition was “real anhydrous”. As to our experiments, the sealed gold capsules were compressed completely with minimum dead volume at 50 MPa during heating. As a considerable amount of water can be produced at the early stage of kerogen degradation,^{8,50,52,53} the water concentration in the compressed capsules for the kerogen alone was actually considerable. Monthieux et al.^{8,9} demonstrated that no significant variations were observed between the pyrolysis experiments on coal with and without the addition of water in a confined system (gold capsules). In their experiments, the amount of water added in the capsules was small (water/OC ratio 0.5–0.7).^{8,9} Therefore, there was no significant difference in the geochemical conditions between these experiments with and without the addition of water. Furthermore, their conclusions were only based on the analytical data obtained from solid residues and Soxhlet extracted bitumen (saturated and aromatic fractions).^{8,9} However, Seewald et al.³⁷ found that CO₂ was continuously generated in large amounts with temperature and heating time increasing and the amount of oxygen in the CO₂ exceeded the oxygen content of the initial kerogen, indicating the incorporation of water derived hydrogen and oxygen into gas hydrocarbons and carbon dioxide. They carried out their experiments under extremely high water/OC ratio (> 25), higher than that in our experiments, to guarantee only aqueous phase and solid sample present in the reaction cell.³⁷

In mineral catalysis experiments, the amounts of the gas hydrocarbons depended on the maturity of the kerogen. In general, the higher the maturity, the higher the amount of gas hydrocarbons. On the basis of molecular parameters and the amount of bitumen released from kerogen, it can be determined that the maturities were considerably higher in the experiments for kerogen alone, in the presence of water only, and in the presence of kaolinite than in the experiments in the presence of montmorillonite, calcite, and dolomite at the same temperature as that demonstrated in part 3.⁴² However, the amounts of gas hydrocarbons were lower in the experiments for kerogen alone and in the presence of water only (water/OC ratio 1.5) than those in the presence of minerals (water/OC ratio 7–10) at 400 °C and lower than those in the presence of kaolinite, montmorillonite, and calcite at 360 °C (Table 1 and Figures 3

and 4). These results may also imply that the incorporation extent of water derived hydrogen and oxygen in hydrocarbons and CO₂ would be lower in the experiments for kerogen alone and in the presence of water only than in the presence of minerals or that oxygen in kerogen would be released preferentially as H₂O in the former (water/OC ratio 0–1.5) and CO₂ in the latter (water/OC ratio 7–10). The result that the amount of gas hydrocarbons was higher in the experiment for kerogen alone than that in the presence of water (water/OC ratio 1.5) at 400 °C appeared to be the only exception, inconsistent with our generally observed trend (Table 1 and Figures 3 and 4).

The recent study by Larsen and Hu demonstrated that the amounts of CH₄ and CO₂ produced in hydrous pyrolysis of kerogen are higher in the presence of pyrite than in the absence of pyrite, and they further increased with the addition of iron-bearing mineral mixtures (FeS, FeS₂, and Fe₃O₄).⁵⁴ It is clear that iron-bearing minerals can enhance the hydrous pyrolysis reaction of a kerogen.⁵⁴ In our study, kerogen was not treated with CrCl₂ to remove pyrite. The result that the amounts of both the gaseous hydrocarbons and CO₂ increase with water/OC ratio can also be ascribed to the fact that the influence of pyrite in hydrous pyrolysis of kerogen was strengthened with water/OC ratio. The result that the amounts of both H₂S and H₂ produced in kerogen pyrolysis increased with water/OC ratio may indicate that pyrite was directly involved in the reaction with organics and water (Figure 7).

Implication for Nature System. Ratios of *iC₄/nC₄* and *iC₅/nC₅*. Numerous studies have discussed the ratios of *iC₄/nC₄* and *iC₅/nC₅* in the subsurface.^{34,55–60} Hunt⁵⁶ carried out a study on light hydrocarbons in sediments (cuttings) from a well drilled off the shore of South Padre Island, Texas, and found that the ratio of *iC₅/nC₅* increases from 0.21 to 0.5 at the surface to a peak of 2–5 at about 2.4 km and then decreases. This peak is approximately at the threshold of increased hydrocarbon generation, and a similar peak is observed in the ratios of *iC₄/nC₄* and 2-methylpentane/*n*-hexane in the Gulf Coast well.⁵⁶ Hunt⁵⁶ interpreted this phenomenon as that the lower temperature reactions tend to produce the branched chain light hydrocarbons, whereas the higher temperature reactions yield increasing amounts of straight chains. Tannenbaum and Kaplan¹⁷ believed that the reversal of these ratios coincides also with the fast disappearance of expandable clays (smectite) and the corresponding increase of Illite, and the decrease of these ratios, therefore, might reflect the diminishing catalytic effect of the rocks due to the lower concentration of expandable clays. On the basis of the results of our experiments, an additional cause for the reversal of these ratios may be related to the decrease of the water/OC ratio of sediments with increasing burial depth due to compaction. Connan and Cassou⁵⁹ indicated that the *iC₄/nC₄* ratio is higher (>0.80) in immature condensates and lower (<0.80) in high wax crudes and mature condensates. This result may be also ascribed to the difference in water/OC ratio. The immature oil was generated from the shallow source rocks with

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high water/OC ratio, whereas the mature oil was generated from deep source rocks with low water/OC ratio.

Hydrocarbon Potentials of Source Rocks. So far, it is unclear whether the incorporation of water derived hydrogen and oxygen in gas hydrocarbons and CO₂ occurs in natural systems. However, as water is ubiquitous in sedimentary basins, this possibility cannot be excluded. Even if we consider the incorporation as the result of the involvement of iron-bearing minerals in the reaction with organics and water, as suggested by Larsen and Hu,⁵⁴ these minerals, especially pyrite, are always present in source rocks. Our data imply that the effects of these minerals could be promoted with water/OC ratio. In different sedimentary basins, or even within the same sedimentary basin, both the contents of water and total organic carbon can vary substantially in the potential source rocks. As a result, water/OC ratios of source rocks range from <1 to >10. As indicated in our experiments, this ratio can significantly influence the amount and composition of hydrocarbons generated during kerogen pyrolysis. Therefore, the routine parameters, such as total organic carbon content (TOC), H/C and O/C ratios of kerogen, vitrinite reflectance Ro (%), and data obtained from Rock-Eval analyses,⁴⁸ may not be adequate to accurately reflect the hydrocarbon potential of the source rocks. Especially, for sedimentary rocks with low TOC (<1.0%) and high porosity (water/OC ratio >4) where the incorporation of water derived hydrogen and oxygen in gas hydrocarbons and CO₂ may be

favorable, the gas hydrocarbon potential may be substantially underestimated on the basis of traditional theory.^{52,61}

5. Conclusions

The effects of water and minerals (i.e., kaolinite, montmorillonite, calcite, and dolomite) on the gaseous pyrolysates from Kukersite kerogen were demonstrated through pyrolysis experiments in a confined system (gold capsules). The results can be outlined as follows:

(1) The ratios of isobutane/*n*-butane and isopentane/*n*-pentane generally increase with temperature and mineral acidity.

(2) The ratios of ethene/ethane and propene/propane generally decrease with temperature and mineral acidity.

(3) All four ratios of ethene/ethane, propene/propane, isobutane/*n*-butane, and isopentane/*n*-pentane increase with increasing water/OC ratio.

(4) Both the amounts of gaseous hydrocarbons and CO₂ increase with increasing water/OC ratio, demonstrating that water derived hydrogen and oxygen are incorporated into gas hydrocarbons and CO₂ and that the incorporation extent increases with the water/OC ratio.

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