

Research Article

Geochemical Characteristics of Released Organic Matters by Acid Decomposition of Hydrocarbon Source Rocks from Different Sedimentary Basins

Peng Liu ¹, Xiaofeng Wang ¹, Xiaofu Li,² Ting Zhang,³ and Wenhui Liu¹

¹State Key Laboratory of Continental Dynamics, Department of Geology, Northwest University, Xi'an 710069, China

²Sichuan Key Laboratory of Shale Gas Evaluation and Exploration, Sichuan Coal Field Geology Bureau, Chengdu 610073, China

³Key Laboratory of Petroleum Resources Research, Gansu Province, Northwest Institute of Eco-Environment and Resources, Chinese Academy of Sciences, Lanzhou 730000, China

Correspondence should be addressed to Xiaofeng Wang; wangxf@nwu.edu.cn

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It has been acknowledged that carbonate was identified as the source rocks of a series of oil-gas fields worldwide. For evaluating the carbonate source rocks, total organic carbon (TOC) contents act as an important indicator. However, the acid solution, which has been generated during conventional TOC measurements, contain organic matters. Hence, the released organic matters in acid solution during carbonate decomposition may lead to underestimate the hydrocarbon generation potential. In this study, rock-eval pyrolysis technique was applied to bulk rock and residue after acid treatment. Meanwhile, the organic matters in acid solution were measured by Gas Chromatography-Mass Spectrometer (GC-MS) to investigate the geochemical characteristics. In addition, the hydrocarbon generation and alteration of TOC contents of released organic matters by acid treatment were studied by hydrous pyrolysis experiments. The results show that the acid solution contains organic compounds, including n-alkanes, saturated fatty acids and fatty acid methyl esters. Meanwhile, total organic carbon (TOC) contents and hydrocarbon generation potential (S1+S2) significantly decrease for bulk rocks after acid treatment in low maturity samples. Moreover, organic CO₂ (S3) decreased after treating of acid, revealing that acidolysis process can affect and release organic matters containing oxygen-bearing functional groups. The S1, S2, S3, and TOC loss are positive correlation with the proportion of rock loss during acidolysis, indicating that the organic matters in acid solution are associated with carbonate minerals. The organic fractions may exist as adsorption state on the surface of carbonate minerals and (or) exist as organic acid salts. Moreover, the thermal simulation experiments reveal that the organic matter in acid solution, which is not recovered by the conventional measurement approach, could contribute to hydrocarbon generation.

1. Introduction

Recently, a series of oil-gas fields were discovered worldwide and carbonate was identified as the source rocks [1–4]. Source rock evaluation can investigate hydrocarbon generation potential and distinguish source rocks. Generally, total organic carbon (TOC) content acts as an important approach in source rock evaluation. Meanwhile, the rock-eval pyrolysis technique has been widely applied in evaluating hydrocarbon generation potential [5–7], and related index (e.g., HI and

OI) can be calculated by pyrolysis parameters to distinguish the types of kerogen. However, some studies indicated that the types of kerogen, which was obtained from HI and OI, may not always accurate [8–10]. Therefore, the TOC content, pyrolysis parameters, and other evaluation approaches can be utilized in combination to investigate hydrocarbon generation potential source rocks.

During conventional TOC measurement process, the rock was treated by acid to remove carbonate. Then, the residual rock was detected by an element analyzer after

neutralization. The generated acid solution during TOC measurements contains organic matters, including fatty acid and aromatic acid [11]. Previous studies also confirmed that organic acids and asphaltene fractionation can be adsorbed onto the surface of carbonate minerals [12, 13]. Alkane components can be formed from fatty acid degradation and the presence of CaCO_3 may promote the degradation by thermal-catalytic effects [14, 15]. Hence, the released organic matters by carbonate decomposition may act as an important role for hydrocarbon generation. Meanwhile, the temperature-programmed pyrolysis can be conducted on source rock samples by a rock-eval pyrolysis instrument to evaluate the source rocks. Pyrolysis products at different assigned temperatures were measured and presented as mg/g, mainly including S1, S2, S3CO, S3'CO, S3 and S3'. Generally, S1, S2, and S3 represent generated hydrocarbon at different temperatures; S3CO and S3'CO correspond to organic CO and CO by reaction of inorganic CO_2 and organic carbon, respectively. In addition, S3' represents mineral origin [5, 6]. Hence, the different pyrolysis products at varying assigned temperatures during temperature-programmed pyrolysis indicate different origins. Bulk rock sample and residue after acid treatment can conduct rock-eval pyrolysis, and related pyrolysis parameters can be obtained. The pyrolysis parameters, which presents as mg/g, can be normalized in initial bulk rocks. Therefore, the difference and alteration for pyrolysis products in bulk rock and residue after acid treatment can be obtained. The difference and alteration in initial bulk sample-normalized pyrolysis parameters for bulk rock and residue samples after acid treatment can reflect the geochemical and hydrocarbon generation characteristics of released organic matters by acid treatment.

In this study, carbonate sample and the residue after acid treatment were conducted by rock-eval pyrolysis experiments and the pyrolysis parameters were normalized to mg in 1 g initial bulk rock. The results for bulk rock and residue after acid treatment were compared to investigate the probably occurrence states of released organic matters. Meanwhile, the organic matters in acid solution were measured to study the organic components and geochemical characteristics. In addition, the relationship of hydrocarbon yields and alteration of TOC contents of acid released organic matters during hydrocarbon generation were investigated by hydrous pyrolysis experiments.

2. Samples and Experiments

2.1. Samples. Hydrocarbon source rocks were collected from different basins in order to obtain samples with different maturity levels. Fresh rock samples were collected and utilized in this study in order to avoid the influence of weathering. Ten outcrop samples (YDGZ-08, YDGZ-09, QT-16, CJG-27, WHSX-17, CJG-40, CJG-17, LMD-15, QT-14, and WHSX-09) with high maturity levels and carbonate contents, including shale, marlstone and carbonate, were collected from Pingliang Formation, Majiagou Formation and Wulalike Formation of Middle Palaeozoic

in Ordos Basin. Mudstone in Pingliang Formation is distributed in the south margin of Ordos Basin and characterized by large thickness, high TOC and high maturity level. Carbonate in Majiagou Formation is widely distributed in the Ordos Basin. Majiagou carbonate rocks were of low TOC and high maturity level. The carbonate in Wulalike Formation is distributed in the northwest margin of Ordos Basin. In addition, eight outcrop samples with low maturity levels and high carbonate contents were collected from different petroliferous basins worldwide. One shale sample (YJG) was collected from Yuejingou area of Lucaogou Formation, Upper Permian of Santanghu Basin. Moreover, five carbonaceous outcrop samples (Eagle Ford-01, 03, 06, 08, 09) were collected from Cretaceous Eagle Ford Formation in Texas, USA. One shale sample was collected from Green River Formation, Washakie Basin, USA, and one shale sample was collected from Woodford Formation, Anadarko Basin, USA.

2.2. Experiments

2.2.1. Acid Treatment of Hydrocarbon Source Rocks. The acid treatment of hydrocarbon generation source rocks in this study includes the following steps: (1) ~10 g sample was ground to 100 mesh, and the mass of sample was quantified exactly (m_1). (2) Then, the samples were transferred to a beaker, and excessive hydrochloric acid (concentration: 6 mol/L) was added to the beaker at room temperature, repeating the above process until no bubbles occur. (3) The residual of rocks in the beaker was static settlement for 24 h to separate the floats, acid solution and rock residues. After finishing the process of static settlement, the floats and acid solution in the beaker were removed and transferred to other two beakers. (4) The beaker with residual of rocks was added deionized water, and after resting rock residues for 6 h, the solution was removed and transferred to the beaker with acid solution in step (3), repeating the above process until the solution is neutral. (5) The beaker with residual of rocks was dried by water bath at 85°C, and the mass of rock residue was quantified exactly (m_2).

2.2.2. Rock-Eval Pyrolysis for Natural Rock Samples, Acid-Treatment Residue. The natural rock samples and acid-treatment residue were conducted by rock-eval pyrolysis experiments by a Rock-eval 6 pyrolysis device (DELSI, France). Different pyrolysis parameters for initial rock and residue after acidolysis can be obtained and normalized to bulk samples by their weights (m_1 and m_2).

2.2.3. Measurements of Organic Compounds by GC-MS. Three shale samples with low maturity level, including Eagle Ford-06, Eagle Ford-09, and YJG, were treated by hydrochloric acid (6 mol/L) for 48 h. Then, the organic compounds in acid solution were extracted by ethyl alcohol.

The organic compounds in diethyl ether were analyzed and determined by a 5973 N mass spectrometer (Agilent Technologies, USA) coupled with a 6890 N gas chromatograph (Agilent Technologies, USA) equipped with a HP-5MS column (30 m × 0.25 mm i.d.). The GC oven temperature was initially set at 80°C, then increased to 300°C at a rate of

TABLE 1: The results of rock-eval pyrolysis for bulk rock samples.

Sample no.	Mass (g)	S1 (mg/g)	S2 (mg/g)	T_{\max} (°C)	S3CO (mg/g)	S3'CO (mg/g)	S3 (mg/g)	S3' (mg/g)	PC (%)	RC (%)	TOC (%)
YDGZ-08	10.03338	0.14	2.33	442	0.02	0.3	0.14	5.8	0.22	0.33	0.55
YDGZ-09	10.09450	0.15	2.62	443	0.01	0.4	0.08	4.3	0.24	0.30	0.54
QT-16	10.00750	0.03	0.83	443	0.05	0.2	0.67	3.4	0.10	0.31	0.41
CJG-27	11.21627	0.03	0.04	416	0.02	0.1	0.18	6.1	0.01	0.07	0.08
WHSX-17	10.02783	0.02	0.04	535	0.03	0.2	0.54	2.5	0.03	0.69	0.72
CJG-40	11.65212	0.03	0.04	312	0.02	0.3	0.19	3.0	0.02	0.46	0.48
CJG-17	10.00444	0.02	0.04	450	0.01	0.1	0.14	5.6	0.01	0.04	0.05
LMD-15	10.09476	0.10	0.68	456	0.13	0.4	0.57	4.0	0.09	0.70	0.79
QT-14	10.54772	0.06	1.83	442	0.07	0.1	0.26	2.3	0.17	0.33	0.50
WHSX-09	10.50695	0.04	0.13	600	0.04	0.3	0.41	6.3	0.03	1.03	1.06
Eagle Ford-01	10.51204	1.73	39.24	426	0.17	1.5	0.75	11.1	3.46	2.79	6.25
Eagle Ford-03	10.08196	2.91	31.05	432	0.11	1.5	0.66	9.9	2.87	2.81	5.68
Eagle Ford-06	10.12211	2.37	31.02	433	0.09	1.5	0.54	9.8	2.82	2.64	5.46
Eagle Ford-08	9.992090	2.00	24.47	432	0.13	1.3	0.69	10.3	2.25	2.63	4.88
Eagle Ford-09	10.54331	0.63	16.59	430	0.70	0.7	1.80	6.9	1.52	2.33	3.85
Greenriver Fm	10.02148	3.81	120.02	437	1.39	1.4	2.58	14.6	10.44	4.34	14.78
Mid Woodford	10.06213	2.74	41.06	416	0.33	0.9	0.53	11.5	3.68	2.72	6.40
YJG	10.03800	2.58	130.02	446	2.85	1.6	6.41	19.3	11.34	7.79	19.13

4°C/min, and held at 300°C for 30 min. In this study, electron ionization (EI) was set at 70 eV with the ion source temperature of 230°C. A full scan mode (m/z 10 to m/z 650) was applied to detect the organic compounds in diethyl ether solution.

2.2.4. Hydrous Pyrolysis Experiment of Shale with Low Maturity Stage. One shale sample (Eagle Ford-01) and different amounts of deionized water were sealed in a high-pressure vessel. The vessel was heated to the designated temperatures (300°C, 350°C, 400°C, 450°C, 500°C, and 550°C) and maintained for 72 h. After finishing the pyrolysis experiments, both the gas and liquid hydrocarbon were collected and the hydrocarbon in residue samples was extracted to definite total hydrocarbon quantity. TOC values were then determined on these residue samples after the pyrolysis experiments with the conventional TOC measurement. Additionally, new “clay-pate” methods, which has been proposed by Liu et al. [16], were also conducted to compare with the conventional TOC measurement to study the alteration of TOC content of acid released organic matters during hydrocarbon generation.

3. Results and Discussions

3.1. Rock-Eval Pyrolysis for Bulk Rock and Residue after Acidolysis. The results of rock-eval pyrolysis for bulk rock samples before and after acidolysis are shown in Tables 1 and 2. The pyrolysis parameters for bulk rock and residue after acid treatment, including S1, S2, S3CO, S3'CO, S3, and S3', were expressed in mg/g and then normalized to

initial bulk rock. The mass of initial bulk rock and residue after acid treatment is m_1 and m_2 , respectively. Hence, S1, S2, S3CO, S3'CO, S3, and S3' in 1 g bulk rock for initial rock and residue after acidolysis can be calculated. Hence, the alteration of S1, S2, S3CO, S3'CO, S3, and S3' for 1 g bulk rock sample before and after acidolysis can be obtained.

3.1.1. Organic and Inorganic Fractions in Source Rocks. S1, S2, S3CO, and S3, which were expressed as mg/g in initial bulk rock, represent the organic fractions from different sources and genesis types. Above pyrolysis parameters were detailedly investigated in previous studies [5, 6]. Generally, S1 corresponds the amounts of hydrocarbon which can be released as the temperature programmatically increased to 300°C [5]. Quantification of S2 means the hydrocarbon generated by cracking reactions of organic matters at temperature from 300°C to 650°C [5, 6]. S3CO corresponds to the quantity of CO which can be generated from cracking of functional groups linked to the organic matters from 300°C [5]. S3 corresponds to the quantity of organic origin CO₂ from 300°C to 400°C. Figures 1(a)–1(c) and 1(e) show the comparison of S1, S2, S3CO, and S3 for rock samples before and after acidolysis. Generally, S1, S2, S3CO and S3 in bulk rock and residue after acid treatment for low maturity samples are significantly greater than that in high maturity level samples from Ordos Basin. The S1 in initial rock with low maturity level obviously decreased after acidolysis (Figure 1(a)). The decline degree of S1 ranges from 11.1% to 45.4% with an average of 25.2%. Meanwhile, 14.1% of the S2 dropped after acid treatment in average (Figure 1(b)). Whereas, no obvious alteration can be

TABLE 2: The results of rock-eval pyrolysis for rock residues after acid treatment.

Sample no.	Mass (g)	S1 (mg/g)	S2 (mg/g)	T_{\max} ($^{\circ}\text{C}$)	S3CO (mg/g)	S3'CO (mg/g)	S3 (mg/g)	S3' (mg/g)	PC (%)	RC (%)	TOC (%)
YDGZ-08	8.64502	0.10	2.83	440	0.04	0.3	0.04	0.6	0.25	0.38	0.63
YDGZ-09	8.49757	0.10	2.73	440	0.03	0.3	0.02	0.7	0.24	0.39	0.63
QT-16	7.85944	0.05	2.07	436	0.15	0.2	0.20	0.6	0.19	0.40	0.59
CJG-27	4.50155	0.06	0.09	353	0.01	0.2	0.58	64.9	0.03	0.32	0.35
WHSX-17	9.80758	0.01	0.03	502	0.13	0.3	0.63	1.5	0.03	0.66	0.69
CJG-40	7.64322	0.03	0.05	505	0.03	0.2	0.11	0.5	0.02	0.56	0.58
CJG-17	5.03215	0.13	0.22	385	0.01	0.2	0.47	91.2	0.05	0.54	0.59
LMD-15	7.89032	0.11	1.05	449	0.20	0.6	0.19	0.8	0.12	0.99	1.11
QT-14	8.74904	0.17	2.78	437	0.09	0.2	0.07	0.3	0.25	0.24	0.49
WHSX-09	5.31117	0.08	0.21	526	0.09	0.6	0.39	0.9	0.05	2.08	2.13
Eagle Ford-01	3.77543	4.03	101.02	426	0.56	0.6	0.38	1.4	8.77	6.46	15.23
Eagle Ford-03	3.14897	6.23	83.11	433	0.34	0.5	0.44	1.5	7.45	6.56	14.01
Eagle Ford-06	4.38627	4.09	64.43	432	0.39	1.3	0.60	2.1	5.75	5.24	10.99
Eagle Ford-08	2.86912	3.80	57.51	436	0.37	1.2	0.55	3.4	5.15	5.26	10.41
Eagle Ford-09	4.59458	2.08	33.27	423	1.26	0.6	2.65	3.0	3.07	4.37	7.44
Greenriver Fm	6.11270	4.25	154.51	438	2.45	0.6	2.61	2.2	13.37	4.82	18.19
Mid Woodford	4.06267	5.86	98.61	421	0.81	0.9	0.71	1.6	8.74	5.64	14.38
YJG	7.17635	3.21	165.41	448	3.73	1.9	6.10	5.3	14.36	8.24	22.60

observed in S1 and S2 in high maturity level samples from Ordos Basin after acidolysis. The S3 decreased significantly after acidolysis in all hydrocarbon source rock samples (Figure 1(e)). 70.1% of the S3 in high maturity samples and 55.2% of the S3 in low maturity samples were lost during acidolysis. However, no obvious change can be observed in the organic CO (S3CO) during pyrolysis for initial rocks (Figure 1(c)).

S3'CO corresponds to the quality of CO which is generated by chemical reaction of CO₂ from decomposition of carbonate and organic carbon with organic source. The reduction process can be described as following:



Two CO molecules can be produced by the reduction reaction of one CO₂ molecular and one carbon atom, indicating that one of the generated CO molecules is of organic origin and another CO molecular is of mineral origin. In addition, S3' corresponds to the quantity of CO₂ with mineral origin generated from 400°C. Figures 1(d) and 1(f) present the comparison of S3'CO and S3' for initial rock samples before and after acidolysis. The results show that S3'CO and S3' in bulk rock and residue after acid treatment for low maturity samples are clearly greater than that in high maturity samples from Ordos Basin. S3'CO in initial rock samples obviously decreased after acidolysis except for five samples from Ordos Basin (WHSX-09, WHSX-17, CJG-17, LMD-15, and QT-14) (Figure 1(d)). The decline degree of S3'CO ranges from 13.8% to 89.6% with an average of 51.6%.

Meanwhile, 86.1% of the S3' dropped after acid treatment in average with the exception of two samples from Ordos Basin (CJG-17, CJG-27) (Figure 1(f)).

3.1.2. Alteration of Total Organic Carbon (TOC) and Hydrocarbon Generation Potential (S1+S2) by Acid Treatment. The TOC content can be calculated by organic fractions during programmed pyrolysis. Figure 2 shows the comparison of bulk rock-normalized TOC contents for initial rock samples before and after acidolysis. Generally, the TOC contents for low maturity samples are obviously greater than that of high maturity samples. Generally, 19.1% of TOC content for low maturity samples decreased after acidolysis (Figure 2), whereas, no obvious decrease can be observed for samples from Ordos Basin due to the low TOC contents and high maturity levels.

Figure 3 shows the alteration of bulk rock-normalized hydrocarbon generation potential (S1+S2) after acidolysis. The alteration of S1+S2 presents a similar characteristics compared with TOC content. The S1+S2 in low maturity samples is significantly greater than that of high maturity samples from Ordos Basin. Generally, 18.5% of the S1+S2 dropped after acidolysis averagely in low maturity samples (Figure 3).

3.2. Geochemical Characteristics of Organic Compounds in Acid Solution. The TIC, m/z 57, m/z 60, and m/z 74 mass chromatograms of the organic compounds extracted by diethyl ether of three low maturity samples (Eagle Ford-06, Eagle Ford-09, and YJG shale) after acidolysis are presented in Figures 4–7, respectively. Generally, the total ion chromatogram was dominated by middle-long chain n-alkanes with carbon numbers ranging from C₁₄ to C₃₃₊ (Figures 4

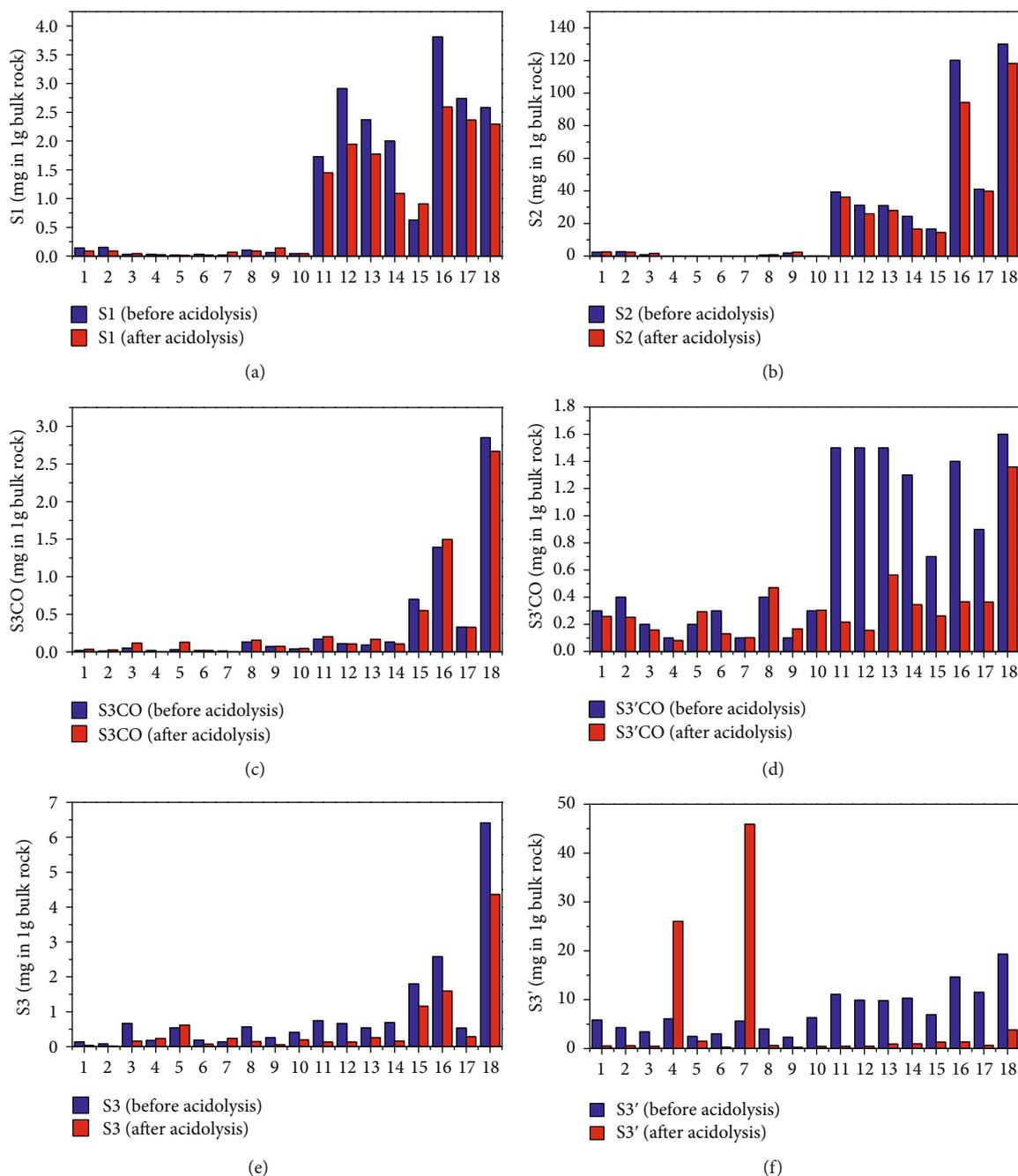


FIGURE 1: Comparison of bulk rock normalized S1 (a), S2 (b), S3CO (c), S3'CO (d), S3 (e), and S3' (f) for initial rock before and after acidolysis. Numbers 1-10 represent the high maturity samples YDGZ-08, YDGZ-09, QT-16, CJG-27, WHSX-17, CJG-40, CJG-17, LMD-15, QT-14, and WHSX-09, respectively. Numbers 11-18 represent the low maturity samples Eagle Ford-01, 03, 06, 08, 09, Greenriver Fm, Mid Woodford, and YJG, respectively.

and 5). The acyclic isoprenoid alkanes are mainly the pristane (Pr) and phytane (Ph) in this study, which are commonly used to assess the redox conditions of depositional environment, and are believed to originate from the phytol side chain on the chlorophyll skeleton in phototrophic organisms [17–19]. Meanwhile, saturated fatty monobasic acids were detected in extraction of acid solution for Eagle Ford-6, Eagle Ford-9, and YJG shale (Figure 6). In general,

the saturated fatty monobasic acids presented the unimodal pattern characteristics with a maximum at C_{9:0}, C_{16:0}, and C_{11:0} for Eagle Ford-6, Eagle Ford-9, and YJG shale, respectively. The detected saturated fatty monobasic acids were characterized by widely carbon number distributions with ranging from C_{6:0} to C_{11:0} in Eagle Ford-6, C_{6:0} to C_{23:0} in Eagle Ford-9, and C_{6:0} to C_{16:0} in YJG, respectively. Moreover, a series of fatty acid methyl esters were detected. The

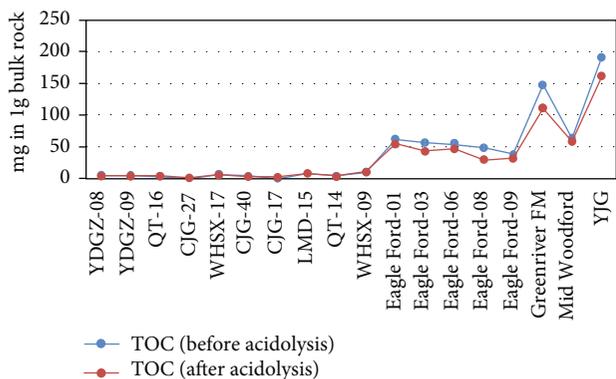


FIGURE 2: Comparison of TOC contents for rock samples before and after treating of acid.

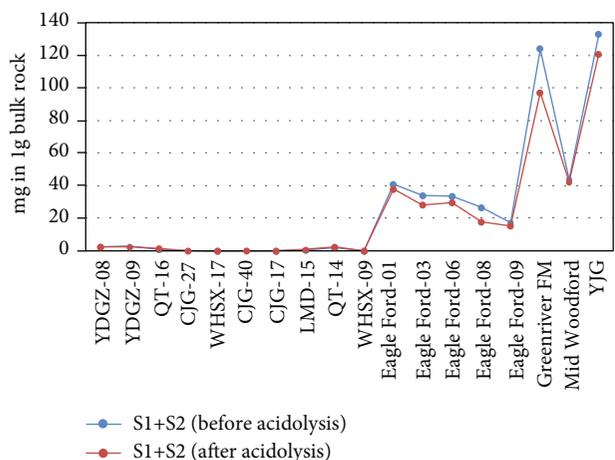


FIGURE 3: Comparison of S1+S2 contents for rock samples before and after treating of acid.

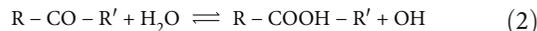
fatty acid methyl esters in Eagle Ford-6 and Eagle Ford-9 were of a maximum at methyl hexadecanoate. Methyl octadecanoate was also detected with a lower content compared with hexadecanoate both in Eagle Ford-6 and Eagle Ford-9 (Figure 7). Meanwhile, phthalic anhydride and methyl phthalic anhydride, which are generated from dehydration reaction between organic acids, were detected in Eagle Ford-6 and Eagle Ford-9 (Figure 7). Therefore, the solution generated during acid treatment of source rocks contains a series of organic compounds, including n-alkanes, saturated fatty acids, and fatty acid methyl esters.

3.3. Geological Significance of Organic Fractions during Programmed Pyrolysis

3.3.1. Different Types of Released Organic Matters. The carbonate minerals, including calcite, dolomite, and siderite, were removed after acidolysis of initial bulk rocks. Figure 8 shows the acidolysis products for samples with different maturity stages. Generally, acidolysis products consist of residue and acid solution in high maturity samples (Figure 8(a)). Whereas, residue, acid solution and solid state floats on

the surface of the solution are three dominating components in acidolysis products (Figure 8(b)), indicating that the released organic matters during acidolysis are different with varying maturity levels.

3.3.2. Geochemical Characteristics of Released Organic Fractions. Bulk rock-normalized S1 and S2 obviously decreased after acid treatment in samples with low maturity stage, suggesting that parts of alkane in S1 are characterized by aqueous soluble and generated S2 also contains hydrophilic organic compounds. Meanwhile, the organic CO₂ (S3) decreased after acidolysis of initial bulk rock, revealing that acidolysis can affect and release organic matter with oxygen-bearing functional groups. The organic matters with oxygen-bearing functional groups can be removed from rocks by acid treatment and may exist as solid state in floats and as dissolved state in acid solution. It is well accepted that the oxygen-bearing functional groups include carboxyl (-COOH), carbonyl (-CO-), formyl (-CHO) and alicyclic (-CO-O-). Meanwhile, the results of GC-MS measurements indicate that the acid solution for three low maturity samples (Eagle Ford-06, Eagle Ford-09, and YJG shale) consists of n-alkanes, saturated fatty acids, and fatty acid methyl esters. Obviously, above organic compounds contain oxygen-bearing functional groups. During acid decomposition, aqueous soluble organic acid and esters can be dissolved in acid solution. Meanwhile, esters can react with water in acidic environment as the following:



Above generated organic acid and alcohols can be dissolved in solution. Hence, the high contents of acid soluble organic matters with oxygen-bearing functional groups in rock can lead to bulk rock-normalized S3 decrease after acidolysis.

Meanwhile, the relationships of proportion of rock loss during acidolysis and proportion of S1, S2, S3, and TOC loss for samples from Cretaceous Eagle Ford Formation in Texas, USA, are presented in Figure 9. The results reveal that the S1, S2, S3, and TOC loss are positive correlation with the proportion of rock loss during acidolysis.

3.3.3. Probable Occurrence States for Acid Released Organic Fractions. Previous studies have investigated the interaction between sea water and carbonate mineral, the results show that no measurable interaction between carbonate mineral and water can be observed due to the organo-carbonate associations, including organic coatings and (or) monomolecular layers on carbonate mineral [20, 21]. Furthermore, the combination and occurrence states for such organic matters with carbonate minerals had been investigated. Chave and Suess [22] have conducted CaCO₃ precipitation experiments in different sea waters, and the results have suggested that the dissolved organic compounds can be adsorbed on the surface of carbonate. Berner et al. demonstrated the humic acids, fulvic acids, aromatic carboxylic acids, and some fatty acids can inhibit the precipitation of carbonate. Meanwhile, affinity of carboxyl groups for Ca²⁺ led to adsorption, which may act

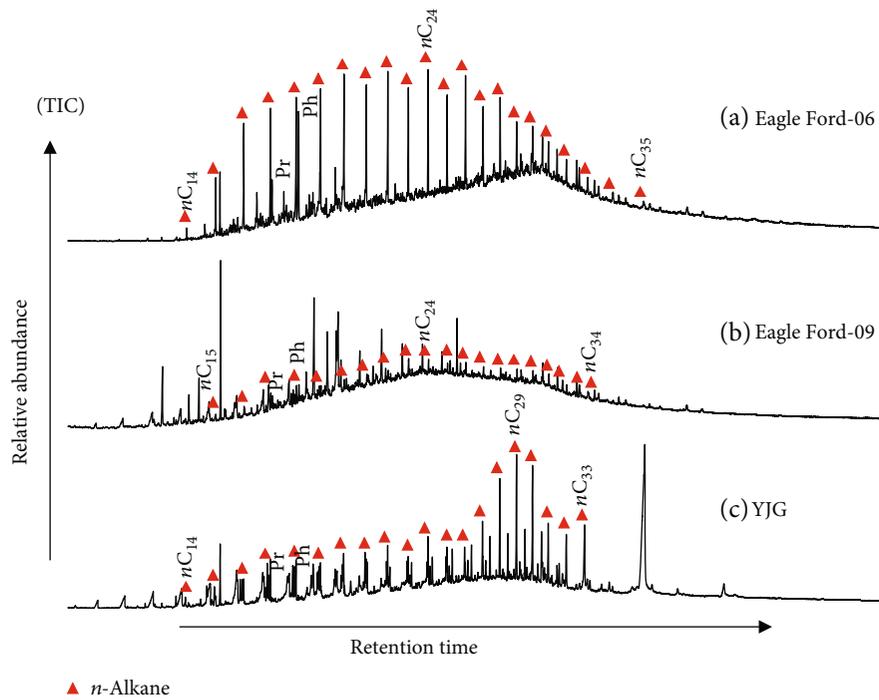


FIGURE 4: Total ion chromatograms of the organic compounds in diethyl ether ((a) Eagle Ford-06, (b) Eagle Ford-09, and (c) YJG).

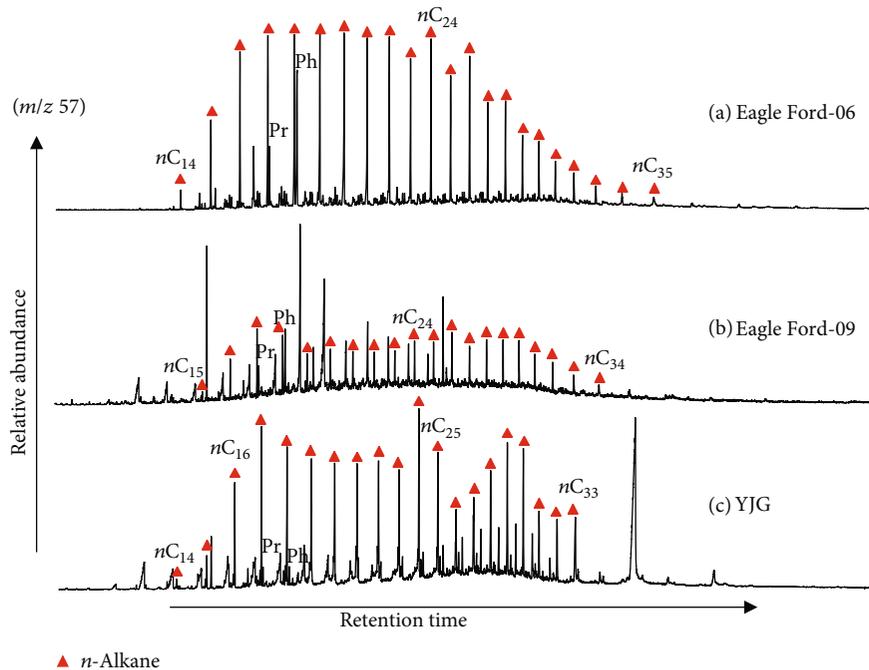


FIGURE 5: m/z 57 mass chromatograms of the organic compounds in diethyl ether ((a) Eagle Ford-06, (b) Eagle Ford-09, and (c) YJG).

as the leading factor inhibiting the precipitation of carbonate [12]. Based on this, different adsorption experiments of organic acids on carbonate were conducted, including fatty acids, yellow acids, nitric acid, amino acid, and acrylic acid ([23–29]). As an important kind of organic acids, the adsorption process of fatty acids had been investigated by Zullig and Morse [28], the result indicates that the adsorption for fatty

acids on carbonate surface only occurred in fatty acids greater than $C_{12,0}$, and the adsorption processes include chemisorption of carboxyl function with Ca^{2+} (Mg^{2+}) sites and hydrophobic bonding between alkyl chains. Overall, the carboxyl in organic acid, which can be attached to the surface of carbonate mineral, leads to the adsorption and aqueous solubility of organic acids acts as the leading factor

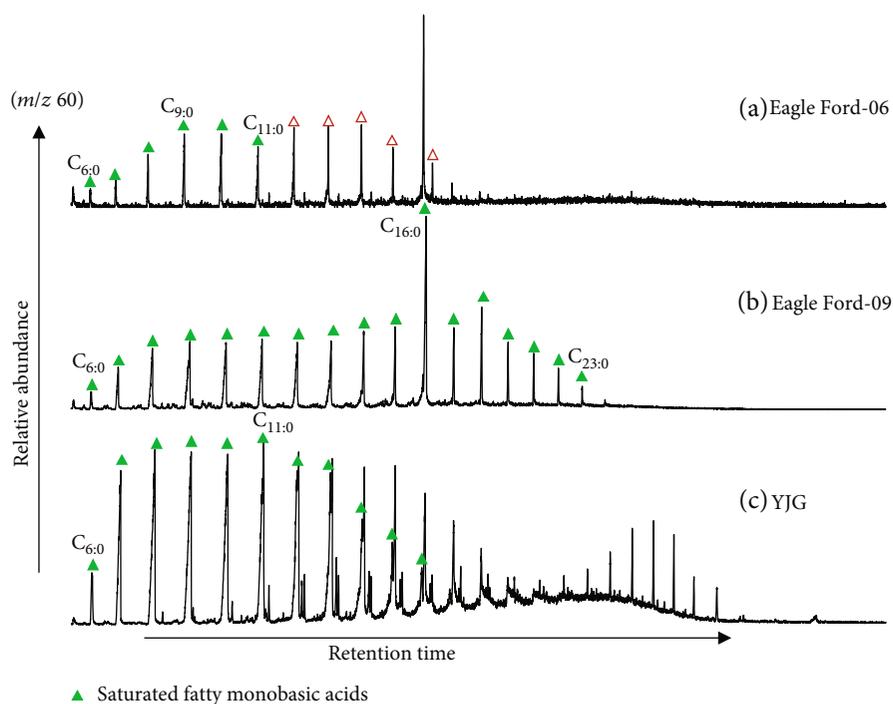


FIGURE 6: m/z 60 mass chromatograms of the organic compounds in diethyl ether ((a) Eagle Ford-06, (b) Eagle Ford-09, and (c) YJG).

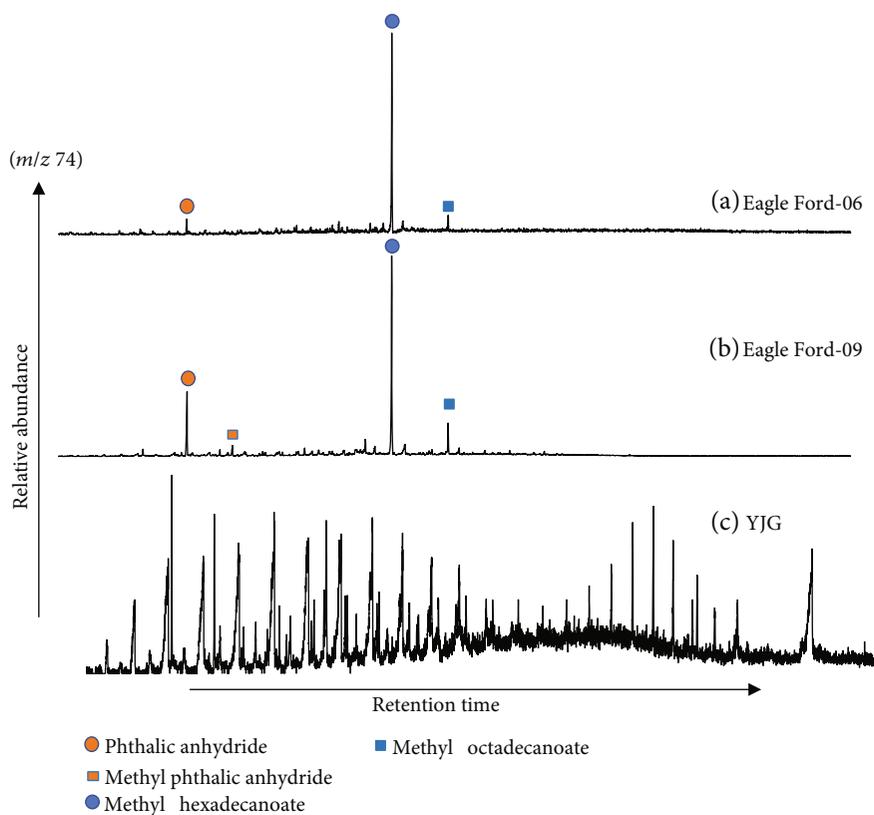


FIGURE 7: m/z 74 mass chromatograms of the organic compounds in diethyl ether ((a) Eagle Ford-06, (b) Eagle Ford-09, and (c)-YJG).

influencing the adsorption process [28]. Meanwhile, the affinity of fatty acids and carbonate increases with increasing alkyl chains [28]. Previous studies also investigated the

adsorption of small carboxy-contained molecular. Geffroy et al. [30] indicated that the small molecules with two carboxyl groups can form a ring complexation with Ca^{2+}

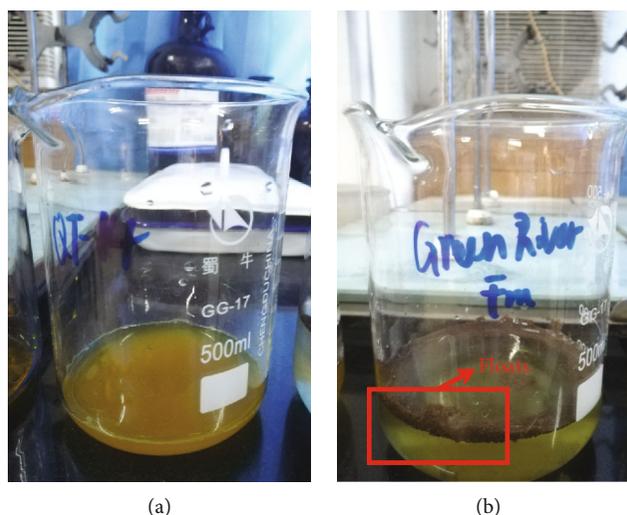


FIGURE 8: Acid treatment products for samples of high maturity level (a) and low maturity level (b).

adsorption sites. Adsorption experiments of malonate and *o*-phthalate were conducted by Li et al. [31] and Li et al. [32], the results suggest that the chemical structure of function groups connected with two carboxyls can influence the adsorption behaviors. Furthermore, molecular simulations were employed to investigate the detailed molecular level adsorption process and mechanism of varying organic acids on the surface of the carbonate minerals, including methanoic acid, poly acrylic acid, alanine, phosphonic acid, and hexanoic acid [26, 33–36]. Double-bonded O in the carboxyl function group can be interacted with Ca atom of carbonate surface directly [34, 35]. In addition, asphaltene fractionation can also be absorbed onto the surface of carbonate minerals [13]. Therefore, the organic compounds with adsorption state can be released to acid solution by removing the carbonate minerals by acidolysis.

Moreover, previous investigations also proved that organic matters can preserve as organic acid salts in carbonate. Wu et al. [37] confirmed that organic acid salts can transfer and deposit with carbonate minerals and maintain a stable state during diagenesis by theoretical calculation. Sun et al. [38] designed an experiment to detect and quantify the organic acid salts in carbonate source rocks. The experimental results reveal that stearate and cetylolate act as the dominating organic acid salts in carbonate rocks [38]. However, saturated fatty monobasic acids were detected in this study by widely carbon number distributions with ranges from $C_{6:0}$ to $C_{11:0}$ in Eagle Ford-6, $C_{6:0}$ to $C_{23:0}$ in Eagle Ford-9, and $C_{6:0}$ to $C_{16:0}$ in YJG shale, suggesting that organic acid salts cannot be completely extracted by proposed approaches. Liu et al. [39] quantified the organic acid salts in source rocks of Ordos Basin by the method proposed by Sun et al. [38], the results indicate that the source rocks with low TOC contents are characterized by high organic acid salt contents, may suggesting that the organic acid salts in carbonate rocks can be generated with increasing maturity stage.

3.4. Contribution of Acid Released Organic Matters to Hydrocarbon Generation. TOC and S1+S2 were usually

applied to evaluate hydrocarbon generation potential [40, 41]. The bulk rock-normalized TOC and S1+S2 for bulk rock and residue after acidolysis indicate that acid treatment leads to hydrocarbon generable organic fraction loss, suggesting that conventional acid-treatment TOC measurements may underestimate the hydrocarbon generation potential. The acid solution, which can be generated during acid treatment, contains organic matters. Meanwhile, a modified TOC measurement method was proposed by Liu et al. [16] and applied to evaluate the source rocks of different maturity stages [42]. In the modified approach, montmorillonite is used to thicken the residue of acid treatment and remaining acid due to the water absorptivity of montmorillonite, revealing that organic matters in acid solution were included in TOC measurement scope.

Hydrous pyrolysis experiment was conducted on a natural sample from Cretaceous Eagle Ford Formation (Eagle Ford-01). Figure 10 shows the yield of total hydrocarbon of the sample in the pyrolysis experiment at 300–550°C. The yield of total hydrocarbon generated peaked at 450°C. The TOC values of the residual samples initially decreased with increasing the temperature of pyrolysis experiments to 400–450°C and then increased with increasing temperature to 500°C, may owing to polycondensation of kerogen. However, the TOC values in the modified measurement are significantly greater than those of the conventional “acid-rinse” method at all temperatures up to 450°C, except at 350°C. The difference could provide information about evolution processes of organic matters released by acidolysis during the pyrolysis. Before 350°C, the conventional TOC value is almost stable, whereas the results of modified measurement decrease with increasing total hydrocarbon yields, revealing that the organic matters released by acid treating can generate hydrocarbon at relatively low temperature. Meanwhile, the difference of TOC values in the two analytical methods decreased above 450°C, indicating that acid soluble organic matters decomposed and produced hydrocarbons. However, it shows no difference in the results of two different TOC analysis

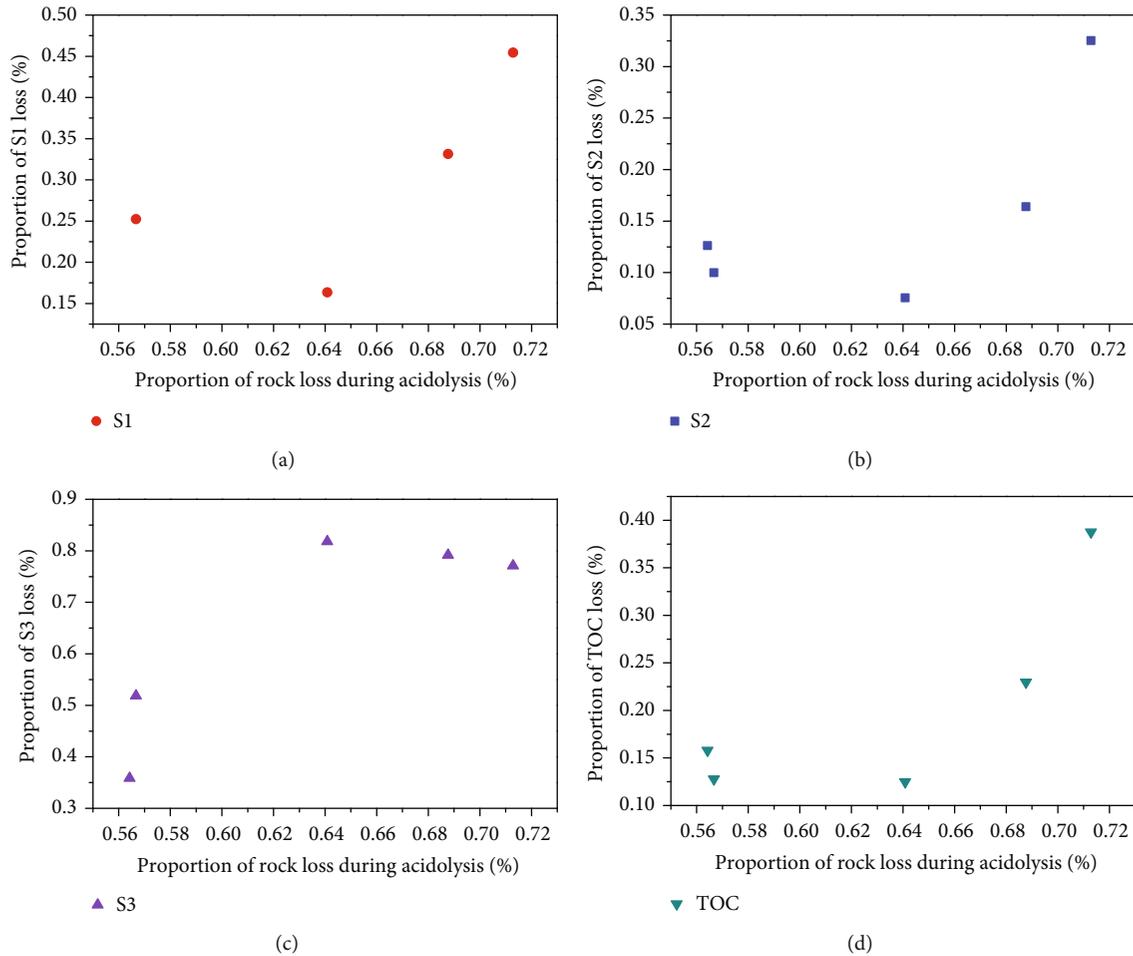


FIGURE 9: Relationships of proportion of rock loss during acidolysis and proportion of S1(a), S2(b), S3(c), and TOC (d) loss for samples from Cretaceous Eagle Ford Formation in Texas, USA.

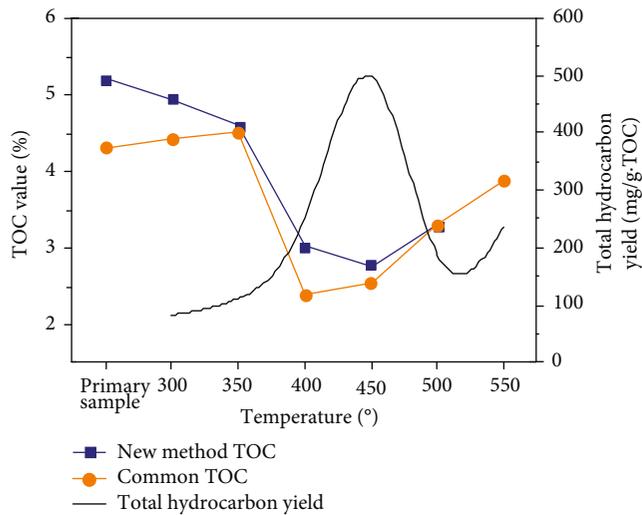


FIGURE 10: Yield of total hydrocarbon in a pyrolysis experiment and the TOC values of residue samples measured by two different TOC test methods. The sample was a low maturity carbonate collected from Cretaceous Eagle Ford Formation in Texas, USA, with the carbonate content of 67%.

methods at 350°C. Those data suggest that the organic matters in acid solution, which contributes to hydrocarbon generation above 350°C, may be reproduced by thermal chemical reactions. Generally, the organic matter in acid solution, which is not recovered by the conventional TOC measurement, could contribute to hydrocarbon generation.

4. Conclusion

In this study, the bulk rock-normalized programmed pyrolysis products for bulk rock and residue after acidolysis were compared to investigate the occurrence states of released organic matters. Meanwhile, the organic matters in acid solution were measured by GC-MS to study the geochemical characteristics. Moreover, the relationship of hydrocarbon generation yields and alteration of TOC contents of acid released organic matters were investigated by hydrous pyrolysis experiments. The major conclusion can be summarized as following:

- (1) S1, S2, TOC contents and S1+S2 significantly decrease for bulk sample after acid treating in low

maturity samples. Meanwhile, organic CO₂ (S3) decreased after treating of acid, revealing that acidolysis processes can affect and release organic matter with oxygen-bearing functional groups

- (2) The solution for acid treatment of hydrocarbon source rock contains a series of organic compounds, including n-alkanes, saturated fatty acids and fatty acid methyl esters
- (3) The S1, S2, S3, and TOC loss are positive correlation with the proportion of rock loss during acidolysis in Cretaceous Eagle Ford samples, revealing that the organic matters in acid solution are associated with carbonate minerals. The above organic fractions may exist as an adsorption state on the surface of carbonate minerals and (or) as organic acid salts in carbonate
- (4) The organic matter in acid solution, which is not recovered by the conventional method, could contribute to hydrocarbon generation

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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