The main generation stage of organic acids during source-rock maturation: Implications for reservoir alteration in deep strata

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Abstract. Generation of short-chain organic acids during source rock maturation was simulated over 72 h, using different kerogens at 220°C–360°C. A Youganwo Formation Type I kerogen sample had the highest organic acid yield (31.0 mg g⁻¹ total organic carbon), twice that of the Yanchang and Kezilenuer formation samples (Type II and III kerogens, ~15 mg g⁻¹). The organic acids were generated mainly in the oil window, regardless of kerogen type. Type I and II kerogen-bearing source rocks produced organic acids with an equivalent vitrinite reflectance (EasyRo) of 1.16%, slightly later than the peak generation of liquid hydrocarbons. Type III kerogen-bearing source rocks produced acids at an early stage (0.95% EasyRo). Most organic acids dissolved in pore waters might have been expelled with hydrocarbons from source rocks containing type I and II kerogen, migrating to reservoirs. Pores and cavities in reservoirs along faults and conduits or near source rocks could be enlarged by mineral dissolution caused by organic acids, with the generated pore space being occupied by the migrated hydrocarbons. During continued burial, these porosities would be preserved, even in deep reservoirs.

1. Introduction

Short-chain organic acids (C₁–C₃) are widely detected in oilfield waters associated with produced petroleum [1, 2]. Total organic acid concentrations reportedly have values of up to 10,000 mg L⁻¹ [1], but concentrations could have been higher in the geologic past if the continual decarboxylation process under certain temperature and geological conditions were considered. Such organic acids are important H⁺ donors and pH buffers in fluids, and may participate widely in organic–inorganic reactions [3, 4]. In reservoirs, they have the ability to dissolve minerals and inhibit mineral precipitation, thus improving reservoir quality [5–7]. Previous experimental studies have demonstrated the importance of organic acids in reservoir alteration. However, as the oxygen-containing functional groups of kerogens are the major source of organic acids [8], a problem confronting petroleum geologists is whether the organic acids generated in source rocks can migrate to reservoirs and contribute to their alteration. Over the last four decades, many studies have simulated the generation of organic acids using different equipment under varied conditions [9–11], although the processes generating the acids are still debated.

In deeply buried reservoirs (>6000 m depth), organic acids could have important roles in pore generation and preservation. Deep strata are thought to exhibit poor reservoir quality, with extremely
low porosity and permeability due to continual compaction. However, some reservoirs at depths of ~8000 m in the Tarim and Sichuan basins of western China are of high quality, with varied concentrations of pores and cavities [12, 13]. Organic acids are among the most active fluids altering these reservoirs, although it is difficult to associate such porous reservoirs with organic acid effects.

In this study, the generation of short-chain organic acids during source rock maturation was simulated using different types of kerogen. All generated organic matter, including gaseous (C1–C3) and liquid (C14+) hydrocarbons, was collected to investigate hydrocarbon generation processes and maturation stages, and to confine the organic acid generation stages. The aims of the study were to describe precisely the generation of organic acids in source rocks, investigate whether these acids could migrate to reservoirs, and to consider their possible roles in the formation of deeply buried reservoirs.

2. Samples and experiments

2.1. Samples

Three immature source rocks containing types I, II, and III kerogen were used in the simulation: Eocene lacustrine shale from the Youganwo Formation (YGW; E2–3y) of the Maoming Basin; Upper Triassic lacustrine shale from the Yanchang Formation (YC; T3y) of the Ordos Basin; and Middle Jurassic coal from the Kezilenuer Formation (KZ; J2y) of the Tarim Basin (figure 1). All were enriched in organic matter with total organic carbon (TOC) contents of 11%–40%. Rock-eval and elemental analyses indicated that all samples were immature (Tmax < 434°C; atomic O/C > 0.10; figure 2a) with high hydrocarbon-generation potential (42 < S2 < 73 mg HC g⁻¹ ROCK; figure 2b). All rocks were crushed to 200 mesh and freeze-dried before use.

The oxygen-containing functional groups in these kerogens were acquired from the 13C NMR spectra using a Bruker AVANCE III 400 MHz NMR spectrometer with Cross-Polarization–Total Sideband Suppression/Magic Angle Spinning (CP–TOSS/MAS) at a 13C frequency of 100.613 MHz.

![Map of China with sample locations](image)

**Figure 1.** General map of China indicating sample locations. YGW, YC, and KZ represent the Youganwo, Yanchang, and Kezilenuer formations, respectively.

2.2. Thermal simulation

Rock powder samples were sealed in gold tubes with deionized water and heated to 220°C–360°C for 72 h under a confining pressure of 50 MPa. Three tubes were used for each temperature: one of 100 mm length to collect water for quantitative analysis of organic acids, and another of 60 mm length for analysis of gaseous, and liquid hydrocarbons. Equivalent vitrinite reflectance was calculated using the ‘EasyRo’ method [14].

2.3. Instrumental analysis

The gold tube of 60 mm length was pierced to allow gas flow into a customized vacuum line connected to an Agilent 7890 gas chromatograph (GC) for determination of gas composition. The tube was opened and ultrasonically extracted with dichloromethane. Liquid hydrocarbons were weighed after a
dehydration and drying process [15, 16]. The large tube of 100 mm length was opened, immersed in 9 mL deionized water, and organic acids extracted for analysis by ion chromatography ( Dionex ICS900), using an AS15 ion-exchange column (4 mm × 250 mm) and KOH eluent. The KOH flow rate was maintained at 1.0 mL min−1 with a gradient elution program [17]. Four organic acids were quantified: formate, acetate, propionate, and oxalate.

**Figure 2.** Organic geochemical characteristics of the three source rocks. (a) atomic H/C vs atomic O/C ratios; (b) S2 vs TOC. Formation definitions as in Figure 1.

3. Results and discussion

3.1. Hydrocarbon yields

The YGW sample (Type I kerogen) produced the highest yield of liquid hydrocarbons (534 mg g−1 TOC), while the KZ sample (Type III kerogen) produced the lowest yields of 12 mg g−1 TOC (figure 3a–c). The YC sample (Type II kerogen) produced intermediate yields of 202 mg g−1 TOC, respectively (figure 3b). The gas yield decreased in the order YC (208 mg g−1 TOC) > YGW (157 mg g−1 TOC) > KZ (34 mg g−1 TOC).

Both the YGW and YC samples reached their maximum yield of liquid hydrocarbons at 0.95% EasyRo, and their gas yields increased gradually in the simulation. The KZ sample displayed a continual increase in liquid hydrocarbon yields with increasing EasyRo, with peak gas generation at 1.34% EasyRo (figure 3c). Based on the classification scheme of maturity stages of Tissot and Welte [18] and our data, the maturation stage can be divided into the oil window (0.6% < EasyRo < 1.3%) and condensate–wet gas (>1.3% EasyRo) stages.

3.2. Organic acid yields

The major organic acid generated at all temperatures was acetate, and the modal proportion of all acids was >83%, consistent with earlier studies [9–11]. The YGW samples had the highest total acid yield of 31.0 mg g−1 TOC, twice that of the YC and KZ samples (13.3–15.4 mg g−1 TOC; figure 3a–c).

Compared with previous simulations, the YGW sample generated a higher yield of organic acids than other samples containing type I kerogen (9.3–14.2 mg g−1 TOC [10]). The maximum yields from YC and KZ samples were within the ranges previously reported for samples containing type II and III kerogen (5.0–22.6 and 13.1–67.7 mg g−1 TOC, respectively [9–11]), although our KZ sample yields were near the lower boundary of previously reported maximum yields. Previous studies have indicated that oxygen-containing functional groups in kerogens may be broken down during the maturation process, forming carboxylic acids. In this study, however, the highest yield of organic acids was not generated from the KZ sample with the highest oxygen (atomic O/C = 0.24) and carboxyl–carboxyl functional group contents (4.5%, figure 4). The generation mechanism for organic acids is thus still unclear, and a detailed investigation of different oxygen-containing functional groups of kerogens is necessary, particularly concerning their relationship with organic acid generation.
3.3. Organic acid generation

Organic acids from the YGW and YC samples reached their maximum yields at 1.16% EasyRo, following peak liquid hydrocarbon generation at 0.95% EasyRo. Organic acids from the KZ sample reached their maximum yield at 0.95% EasyRo, at which small amounts of gas were still being generated.

Our results are not consistent with the view that kerogen generates organic acids in large amounts before entering the oil window [18]. Previous studies observed coupled generation of organic acids and liquid hydrocarbons, and concluded that the maximum yield of organic acids may occur in the oil window or during later stages of maturation, but failed to confirm the precise stage [19]. This study conclusively demonstrates that organic acids are generated mainly in the oil window, regardless of the organic matter type.

3.4. Migration of organic acids from source rocks to reservoir

During the maturation process, pore fluid pressure in source rocks containing type I and II kerogen may increase sharply, and both pore water and liquid hydrocarbons can be expelled. At that time, organic acid content in pore water would be near maximum, and they could migrate into the reservoir along with expelled petroleum. In coal, most organic acids formed prior to gas generation could be partly decarboxylated to CO\(_2\) [20], and would thus be unable to migrate into the reservoir; however, organic acid migration from coal to reservoirs is possible in some situations e.g., when a source rock is buried rapidly, as occurred in the Kuqa Depression, Tarim Basin, and the generation window for organic acids and gas is short. Under these conditions, organic acids derived from coals can migrate into reservoirs together with generated gas.
3.5. The role of organic acids in deeply buried reservoirs

Organic acids may be most likely to contribute to reservoir alteration in the poriferous spaces along conduits or near source rocks, also known as ‘injection points’ where hydrocarbons enter reservoirs. Organic acids could dissolve both crystal and matrix minerals and further enlarge existing pores and cavities. With continued injection of hydrocarbons, the enlarged spaces would become fully occupied by hydrocarbons, with waters containing dissolved minerals migrating downward. In deeply buried reservoirs, the layer occupied by hydrocarbons may sustain good reservoir quality, but the water layer could become blocked through mineral precipitation and decarboxylation of organic acids in high-temperature environments. The occurrence of high-quality reservoirs in deep strata is therefore possible.

In the craton of the Tarim Basin, vertically developed faults, including NE-striking strike–slip faults and NW-striking thrust faults, provided the major upward-migration conduits for hydrocarbons. In some deep strata (>6000 m depth), a specific type of reservoir known as a ‘fault-karst’ reservoir was recently discovered, with cavernous spaces along these faults [12, 13]. Development of these spaces was suggested to be related to deep-source, upward-migrating hydrothermal fluids [13]. The organic acid-enriched fluids from source rocks could be a significant component of such fluids, although further field studies are required to confirm this.

4. Conclusions

In the simulation involving source rocks containing different kerogen types, the generation and yields of short-chain organic acids in oilfield waters led to the following conclusions.

1) YGW samples (Type I kerogen) produced the highest yield of organic acids (31.0 mg g\(^{-1}\) TOC), twice that of the YC and KZ samples (Type II and III kerogens, ~15 mg g\(^{-1}\) TOC).
2) Organic acids were generated mainly in the oil window, slightly later than peak liquid hydrocarbon generation from type I and II kerogen-bearing source rocks, but before significant gas generation from Type III kerogen-bearing source rocks.
3) Organic acids dissolved in pore waters may be expelled from source rocks containing type I and II kerogen together with oils, migrating to reservoirs. Migration of organic acids to reservoirs from source rocks containing Type III kerogen is also possible when the generation window for organic acids and gas is time-constrained (e.g., when the source rock is rapidly buried).
4) Organic acids can alter the reservoir preferentially along conduits or near source rocks. They can carry dissolved ions and migrate downward, avoiding mineral precipitation in the oil layer. With deeply buried reservoirs, such spaces would be well preserved in hydrocarbon layers.

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References

[1] Seewald J S 2003 Nature 426 327-333.
[2] Carothers W W and Kharaka Y K 1978 AAPG Bulletin 62 2441-2453.
[3] Surdam R C and Yin P 1994 Organic acids and carbonate stability, the key to predicting positive porosity anomalies Organic Acids in Geological Processes ed E.D. Pittman and M.D. Lewan (Berlin, Heidelberg: Springer) chapter 13 pp 398-448.
[4] Meshri I D 1986 On the reactivity of carbonic and organic acids and generation of secondary porosity Roles of organic matter in sedimentary diagenesis ed D.L. Gautier (United States: SEPM Special Publication) pp 123-128.
[5] MacGowen D B and Surdam R C 1990 Importance of organic-inorganic reactions to modeling water—rock interactions during progressive clastic diagenesis Chemical Modeling of Aqueous Systems II ed D.C. Melchior and R.L. Bassett (Washington, DC: American Chemical Society) chapter 38 pp 494-507.
[6] Harrison W J and Thyne G D 1992 *Geochimica et Cosmochimica Acta* **56** 565-586.
[7] MacGowan D B and Surdam R C 1990 *Applied Geochemistry* **5** 687-701.
[8] Lewan M D and Fisher J B 1994 Organic acids from petroleum source rocks *Organic Acids in Geological Processes* ed E.D. Pittman and M.D. Lewan (Berlin, Heidelberg: Springer-Verlag) chapter 4 pp 70-114.
[9] Andresen B, Thronsden T, Barth T and Bolstad J 1994 *Organic Geochemistry* **21** 1229-1242.
[10] Dias R F, Freeman K H, Lewan M D and Franks S G 2002 *Geochimica et Cosmochimica Acta* **66** 2755-2769.
[11] Knauss K G, Copenhaver S A, L. Braun R and Burnham A K 1997 *Organic Geochemistry* **27** 477-496.
[12] Li Z, Huang S, Liu J, Cai C, Li Y, Li K, Han Y and Zhao Y 2010 *Acta Geologica Sinica* **28** 969-979.
[13] Li Z, Li J, Zhang P W, Yu J, Liu J and Yan L 2016 *Bulletin of Mineralogy, Petrology and Geochemistry* **35** 827-838.
[14] Sweeney J J and Burnham A K 1990 *AAPG Bulletin* **74** 1559-1570.
[15] Wang Q, Jia W, Yu C, Song J, Zhang H, Liu J and Peng P 2020 *Energy & Fuels* in press.
[16] Jia W, Wang Q, Liu J, Peng P, Li B and Lu J 2014 *Organic Geochemistry* **71** 17-29.
[17] Zhong Y, Yu C and Peng P 2010 *Chinese Journal of Chromatography* **28** 923-928.
[18] Tissot B P and Welte D H 1984 *Petroleum formation and occurrence* (New York: Springer-Verlag Berlin Heidelberg).
[19] Barth T, Borgund A V and Hopland A L 1989 *Organic Geochemistry* **14** 69-76.
[20] Bell J L S and Palmer D A 1994 Experimental studies of organic acid decomposition *Organic Acids in Geological Processes* ed E.D. Pittman and M.D. Lewan (Berlin, Heidelberg: Springer) chapter 9 pp 226-269.