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Current Research Status on the Phase Behavior Evolution of Shale Oil During In Situ Conversion

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Abstract

China possesses abundant shale oil resources, which, despite their overall low maturity, hold significant development potential. In situ conversion technology is the key to the efficient development of these medium-low maturity shale oil resources. Research in this area is a focal point in the oil and gas sector. Studying the phase behavior evolution of organic components during the heating process is crucial for both laboratory simulation and guiding extraction operations. However, comprehensive research methodologies specifically targeting phase behavior evolution during in situ conversion remain scarce, with no mature approach established. This paper begins by reviewing previous explorations and studies on predicting the phase behavior of oil and gas in low-maturity source rocks, detailing the principles, technical key points, and application cases of the Phase Kinetics method, as well as the advantages and improvements of the PhaseSnapShot method. Building upon the previously proposed two methods and considering the reservoir characteristics and hydrocarbon generation features of medium-low maturity shale oil, this paper introduces suitable hydrocarbon generation thermal simulation experiments, pyrolysis product analysis techniques, and equations of state for simulating the in situ conversion process. Finally, it proposes a research methodology for predicting phase behavior tailored to the in situ conversion of medium-low maturity shale oil.

Keywords: shale oil; in situ conversion; phase behavior; pyrolysis; PVTsim; EOS

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1. Introduction

In 2006, shale oil and gas in the United States entered an era of rapid development, marking the beginning of the "Shale Gas Revolution" [1,2], during which shale gas production accounted for more than half of the country's domestic crude oil output [3]. The "Shale Gas Revolution" significantly accelerated the growth of oil production in the United States and reshaped the global energy landscape [4]. China also possesses abundant shale oil resources. In recent years, various institutions have repeatedly estimated China's shale oil reserves and recoverable resources using different methods. According to the third national oil and gas resource assessment and calculated with a 5% recovery factor, the onshore shale oil resources in China's major basins are estimated at 1.86×10^{10} tons [5]. Based on the maturity evolution stages of shale oil, ZHAO Wenzhi et al. [6] classified shale oil into oil shale (Ro < 0.5%), medium-low maturity shale oil (Ro = 0.5–1.0%), medium-high maturity shale oil (Ro = 1.0–1.6%), and shale gas (Ro > 1.6%).

The large-scale development and utilization of retained hydrocarbon resources in medium–high maturity shale oil formations primarily rely on horizontal wells and stimulated reservoir volume (SRV) fracturing technologies [7]. However, the development of medium-low maturity shale oil faces challenges due to the coexistence of retained liquid hydrocarbons, various bitumens, and unconverted organic matter. Horizontal well and fracturing technologies often fail to achieve economical production, while traditional surface retorting methods suffer from low efficiency and significant environmental pollution [8]. Therefore, advancing the development of medium-low maturity shale oil toward in situ conversion processing (ICP) has become an inevitable trend. ICP technology involves heating organic matter within shale formations using underground heating equipment or high-temperature fluids. This process induces in situ pyrolysis of organic matter, generating light oil and natural gas. The produced oil and gas are then lifted to the surface via conventional extraction methods, while leaving behind coke and other impurities underground [9].

The technically recoverable resources of medium-low maturity shale oil in China through in situ conversion are estimated to be approximately (700–900) $\times 10^8$ tons, which is about three to four times the total recoverable resources obtainable by conventional petroleum techniques [10,11]. The breakthrough in underground in situ conversion technology for shale oil will effectively unlock the development and utilization of its vast potential resources. Currently, among China's underground in situ conversion technologies for shale oil, the most advanced ICP technology in China is the horizontal-well electric heating light hydrocarbon upgrading process (Figure 1), jointly developed by the Research Institute of Petroleum Exploration and Development in cooperation with Shell, designed specifically for organic-rich shale reservoirs at burial depths 300 to 3000 m and Ro values of 0.5–1.0% [12,13].

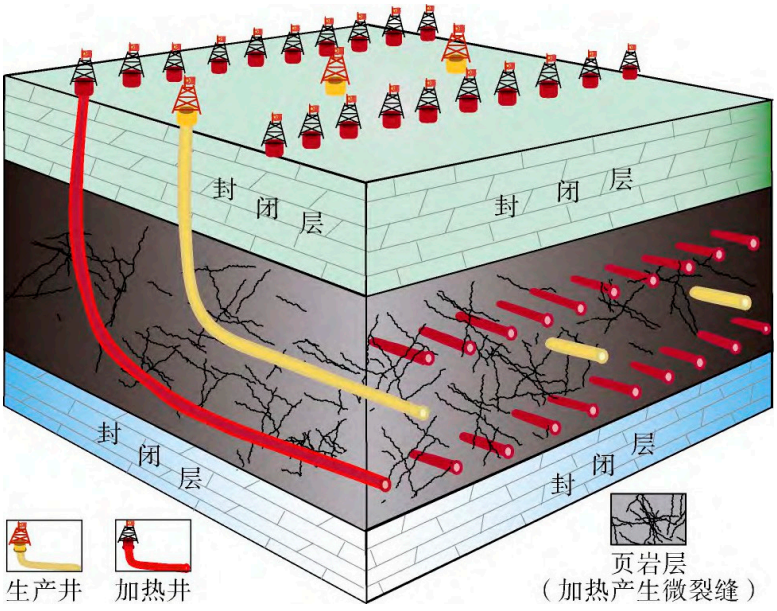


Figure 1. Schematic diagram of the horizontal well electric heating light hydrocarbon upgrading process [13]. (生产井: Production Well; 加热井: Heating Well; 封闭层: Cap Rock/Seal Layer; 页岩层: Shale Formation; 加热产生微裂缝: Microfractures Generated by Heating).

The process of in situ conversion of shale oil involves complex mechanisms of organic matter pyrolysis, with numerous factors influencing the cracking process [14]. In recent years, numerous scholars have investigated the principles of in situ kerogen pyrolysis and the factors and patterns influencing the properties of the produced oil and gas under var-

ious heating conditions through physical experiments and numerical simulations [15–24]. The findings from these physical simulation experiments and numerical simulation studies provide crucial guidance for further exploring the pyrolysis principles underlying shale oil in situ conversion. The essence of in situ conversion pyrolysis is a continuous dynamic chemical reaction process involving the coupling of multiple components and phases. During the heating evolution, heavy components in the products continuously transform into lighter components, while both temperature and pressure constantly change. The chromatographic analysis results of the crude oil produced at different temperatures and pressures show significant differences [18], indicating that the hydrocarbon phase state, phase behavior, and phase equilibrium are all distinct at different stages of the heating process. Studying the phase state, phase behavior, and phase equilibrium of oil and gas can better reveal the characteristics at different thermal maturity stages, such as the primary oil window and the cracking gas window. This understanding provides crucial guidance for determining the optimal heating temperature, heating rate, and pressure for medium-low maturity shale oil.

Conventional PVT apparatus currently cannot replicate the dynamic phase behavior changes during pyrolysis. Consequently, research on the phase behavior of in situ conversion fluids remains scarce, and dedicated methodologies are lacking. For simulating and predicting maturity-induced phase behavior changes in medium–low source rocks, where conventional PVT experiments on produced fluids for well stream analysis are infeasible [25,26], the primary approach involves simulating compositional changes during source rock pyrolysis through close-system or open-system pyrolysis experiments and coupling this experimental data with numerical simulation to predict phase behavior. Thermal simulation experiments are based on the time-temperature compensation principle of organic matter thermal evolution. By conducting high-temperature, short-duration pyrolysis experiments, they can simulate the low-temperature, long-term thermal evolution processes that occur in geological environments [27–30]. Di Primio and Horsfield [31] utilized both open-system and closed-system pyrolysis experiments, combined with modern basin modeling software, to simulate hydrocarbon composition during generation and the phase behavior of fluids during migration. This work led to the development of the Phase Kinetics model, capable of predicting the phase behavior of oil and gas for different organofacies types. Huang et al. [32] simulated the thermal cracking process of crude oil at different maturity stages based on gold-tube closed-system pyrolysis experiments. They utilized numerical simulation software and the Peng–Robinson (PR) equation of state to generate phase envelopes for the oil and gas at varying maturity levels. Shi et al. [33], employing a modified gold tube pyrolysis system, investigated the effects of different pyrolysis pressures on oil cracking and the associated phase behavior changes. Although numerous scholars have integrated thermal simulation experiments, reaction kinetics [24], and phase equilibrium equations [34] with numerical simulation techniques to model the evolution of pseudo-components during in situ conversion heating and pyrolysis, their research often lacks detailed analysis of the quantitative changes in specific components throughout the pyrolysis process [35,36]. Consequently, relying solely on the results of pseudo-component evolution makes it difficult to accurately characterize the phase behavior and its transient changes using numerical phase behavior simulation software [37].

Building upon prediction methods for the phase behavior of fluids in medium–low petroleum systems, this paper investigates a research methodology that utilizes pyrolysis experimental data and phase behavior simulation software to model fluid phase state, phase behavior, and phase equilibrium during in situ conversion. Additionally, it discusses the relevant experimental techniques involved in this approach.

2. Prediction Methods for Hydrocarbon Fluid Composition and Phase Behavior

The composition of hydrocarbons is a key determinant of their phase behavior during migration, accumulation [38], and production [39]. Under any given temperature and pressure conditions, the physical state of hydrocarbons can be represented by a phase envelope. Based on the shape of this envelope and its critical parameters, petroleum fluids are categorized into five classical types: black oil, volatile oil, retrograde condensate gas, wet gas, and dry gas [40,41]. The phase behavior of reservoir fluids critically influences their mobility. Compared to conventional black oil systems, gas, condensate, and volatile oil reservoirs—characterized by higher light hydrocarbon content, lower viscosity, and single-phase flow potential—exhibit superior flow properties. Since the phase behavior evolution of oil and gas is primarily governed by the interplay of fluid composition, reservoir temperature, and pressure [31], the evaluation and prediction of the complete compositional profile of shale oil under geological conditions have become a fundamental prerequisite for scientifically assessing its mobility, predicting phase behavior, and estimating recovery potential. Scholars have already proposed relatively comprehensive methods for predicting petroleum fluid composition and phase behavior, such as the Phase Kinetics (PK) method based on the hydrocarbon generation kinetics of source rocks, and the PhaseSnapShot (PS) method tailored for mature shale regions.

2.1. Phase Kinetics (PK) Method

The Phase Kinetics (PK) method integrates open-system (Rock-Eval) and closed-system (MSSV) pyrolysis to characterize the compositional evolution of fluids generated under increasing thermal stress. It corrects measured gas compositions to overcome systematic biases of traditional pyrolysis techniques—particularly the underestimation of methane and overestimation of ethane and propane—and establishes a quantitative linkage between organic facies and hydrocarbon phase behavior. Based on the "structural moiety approach" concept, the PK method posits that low-polarity compounds in pyrolysis products can characterize kerogen structural features. This enables the prediction of phase equilibrium behavior for petroleum fluids generated under natural geological conditions.

2.1.1. Principles and Technical Framework

Pyrolysis, defined as a chemical cracking process induced solely by heat [42], is ideally suited for investigating the mechanisms of gas and liquid hydrocarbon formation from kerogen in source rocks. By accelerating thermal evolution, pyrolysis experiments reproduce the hydrocarbon generation process from low to high maturity within a short timeframe, allowing simulation of variations in product type and composition at different maturity levels.

- Organic Facies Classification

Based on pyrolysis gas chromatography (Py-GC) results, source rocks are classified into five petroleum-type organofacies (OF1–OF5), including condensate-prone, paraffinic-naphthenic-aromatic (PNA)-type oils (high-wax and low-wax variants), and paraffinic-type oils (high- and low-wax variants) [43]. Each organofacies exhibits specific hydrocarbon generation potential.

- Open and Closed-System Pyrolysis

The rate of petroleum generation is jointly determined by the duration of exposure of source rock kerogen to temperature and the kinetic parameters of its thermal degradation. Since calculating kinetic constants from confined-system experiments requires the analy-

sis of a large number of samples [44], the PK method adopts an approach that correlates changes in sample composition with the transformation ratio (TR), and the transformation ratio is predicted via a petroleum generation model [45].

The PK method uses Rock-Eval 6 to determine the bulk kinetic parameters—including the activation energy distribution and frequency factor—for eight representative samples. Subsequently, the temperatures required for the studied samples to reach transformation ratios (TR) of 10%, 20%, 30%, 50%, 70%, and 90% are determined. Non-isothermal confined-system pyrolysis (MSSV) is then conducted at a heating rate of 0.7 °C/min until the temperatures corresponding to each TR are reached.

Based on the compositions of C_1–C_5 gases and C_6^+ liquids obtained from the MSSV experiments, the evolution trends of the gas–oil ratio (GOR) with increasing maturity (TR) or geological temperature are investigated for different organofacies types. It is ultimately concluded that, under temperature conditions representative of primary cracking, the GOR determined by confined-system pyrolysis closely approximates the natural GOR distribution observed in geological systems.

- Empirical Composition Correction

There are significant differences between the gas composition generated under experimental pyrolysis conditions and that of gases and associated gases formed under natural geological conditions [46,47]. The most notable compositional discrepancy lies in the relatively lower methane content compared to naturally generated gas, coupled with higher ethane and propane contents. As the most abundant compound in the petroleum gas phase, methane also exerts the greatest influence on phase behavior and the saturation pressure of the fluid. At medium-low stages, phase behavior predictions based on non-isothermal MSSV pyrolysis in confined systems align relatively well with actual phase behavior. However, as maturity increases, particularly within the main oil window and late oil window, significant deviations emerge between predicted and actual saturation pressures. These marked differences in gas composition and saturation pressure can lead to substantial inaccuracies in phase behavior predictions.

To address the issue of low methane proportions in pyrolysis gases, the PK method empirically adjusts the composition of the pyrolysis products. It assumes that the ratio of methane to wet gas compounds (C_1/C_{2-5}) increases with the transformation ratio of the kerogen. After applying this adjustment to correct the C_1/C_{2-5} ratio, the resulting gas composition and the relationship between saturation pressure and GOR show better agreement with those of natural fluids.

- Compositional Kinetic Modeling

In a two-component "oil-gas" model, the physical properties of each component remain constant, making it unable to simulate the evolution of fluid physical properties and phase behavior with increasing maturity. The optimal approach for calculating petroleum phase behavior using an equation of state (EOS) also adopts the fluid compositional modeling method commonly used by reservoir engineers. Among the factors influencing oil and gas phase behavior, the composition and molar amount of the gas phase are the primary controlling elements. However, the relative content of heavy versus light compounds in the liquid phase significantly regulates the saturation pressure. When heavy compounds dominate, the solubility between the liquid and gas phases diminishes markedly, consequently leading to an increase in saturation pressure. Therefore, the influence of liquid composition on hydrocarbon phase behavior cannot be overlooked.

PVT simulation software requires comprehensive fluid composition parameters to describe phase behavior: the gas phase must provide the mole fractions of C_1–C_5 n-alkanes and i-alkanes; the liquid phase must include at least the C_6 and C_7^+ fractions. Here, C_6

is typically represented as a single pseudo-component, while the C_7^+ fraction requires additional specification of its mole fraction, molecular weight, and density. Addressing the need for refined shale fluid phase behavior modeling, the PK method utilizes Calsep's PVTsim Nova 3. Based on the carbon number distribution characteristics of shale heavy hydrocarbons, it splits the C_7^+ fraction into multiple pseudo-components: $C_{7–15}$, $C_{16–25}$, $C_{26–35}$, $C_{36–45}$, $C_{46–55}$, and $C_{56–80}$. Finally, the PVT parameters are input into the PVTsim software to conduct the phase behavior simulation.

2.1.2. Applications and Limitations

The authors applied their developed compositional kinetics model to three case studies: the Sonda de Campeche field in Mexico, the Snorre field in the North Sea, and the Reconcavo Basin in Brazil, to predict fluid phase behavior. The study focused on evaluating key parameters such as the gas–oil ratio (GOR), saturation pressure (Psat), and formation volume factor (Bo), comparing the predictions with measured data from natural fluids in the actual reservoirs. The results demonstrate that the model exhibits strong predictive capability across different geological settings and source rock types (e.g., organofacies types OF3b, OF3a, and OF5a). The predicted values for GOR, Psat, and Bo all fall within the range of measured fluid properties, validating its applicability and reliability for predicting medium to high maturity black oil systems.

The PK method successfully achieves an accurate characterization of oil shrinkage behavior and the evolution of saturation pressure, significantly enhancing the reliability of petroleum migration modeling. Furthermore, it incorporates two-phase processes such as phase separation and differential migration into petroleum system modeling, thereby expanding the model's application scope. However, the method has limitations: it only describes the generation of primary cracking products and lacks the kinetic description of secondary oil-to-gas cracking. This leads to significant limitations in predicting high GOR fluids like light oils and gas condensates. Additionally, constrained by basin modeling technology, it struggles to accurately simulate the charging history in complex reservoirs with faults and multi-stage charging (such as the Snorre field), often providing only generalized assessments. Consequently, it is more suitable for petroleum systems with relatively simple structures, dominated by primary cracking products, and where secondary cracking can be neglected. Despite these limitations, the method's compositional resolution of 14 compounds supports the definition of specific cracking parameters for each compound, offering the potential for incorporating secondary cracking reactions in the future.

2.2. PhaseSnapShot (PS) Method

The Phase Kinetics (PK) model is a forward-modeling approach that has been demonstrated to effectively predict the bulk composition and phase behavior of petroleum in numerous conventional marine and nonmarine plays. This model is constructed using immature samples by populating a bulk kinetic model with compositional data obtained from non-isothermal confined-system pyrolysis (MSSV) experiments, formatted for PVT reporting.

Although cumulative compositions from low to high maturity are suitable for modeling expelled fluids in conventional reservoirs, studies have found that instantaneously modeled fluid fractions are better suited for predicting petroleum compositions within shales [48]. From a forward-modeling perspective, the "next-formed" fluids in a shale exhibit a high degree of similarity to the properties of fluids currently observed in a closely located well of slightly higher thermal maturity.

The PhaseSnapShot method is an innovative phase behavior prediction approach proposed for shale petroleum systems. Its core concept involves using a nearby medium-lower

shale sample to simulate the instantaneous composition of the "next-formed" fluids for the target area, thereby overcoming the prediction bias caused by the cumulative effect when applying the traditional Phase Kinetics (PK) model to shales [49].

Improvements in the PhaseSnapShot (PS) Method Technique

PS and PK methods share significant commonalities in their technical pathways and application logic: both have the core objective of predicting the phase behavior and composition of subsurface petroleum fluids, and both rely on laboratory pyrolysis techniques to generate the fluid composition data required for phase behavior simulation. Furthermore, both methods recognize that the gas composition obtained directly from pyrolysis deviates from natural fluids—exhibiting, for instance, lower methane content—and thus require empirical correction of the gas composition to ensure the accuracy of phase behavior predictions. Subsequently, the physical properties and phase characteristics of the fluids are calculated based on an equation of state. Although the Phase Kinetics (PK) and PhaseSnapShot (PS) methods share a similar core technical rationale, significant differences exist between them in terms of applicable reservoirs, sample selection, pyrolysis experiment selection and simulation procedures, fluid composition, and gas correction (Table 1).

Table 1. Comparison of differences in key technical parameters between the Phase Kinetics method and the PhaseSnapShot method.

	Phase Kinetics	**PhaseSnapShot**
Applicable Reservoir	Conventional and Shale Oil Reservoirs	Eagle Ford Shale Reservoir
Sample Selection	Immature or Low-Maturity Source Rocks	Samples Slightly Less Mature than the Target
Pyrolysis Experiment	Open/Closed Pyrolysis	Closed Pyrolysis Experiment
Simulation Process	Simulates the Entire Hydrocarbon Generation Process	Simulates up to the Adjacent Maturity Stage
Fluid Composition	Mixed Fluid of Cumulative Generated Hydrocarbons	Mixed Fluid of Instantaneously Generated Hydrocarbons
Gas Component Correction	Based on Common C_1/C_{2-5} Ratios	Based on PVT Data from the Study Area
Retention Assumption	Does Not Consider Retention Effects	Considers Strong Retention Effects of C_7^+ Components and Free Bitumen
Method Advantage	Provides a universal prediction framework from source rock organic facies to generated fluid types, suitable for basin-scale modeling.	Offers more accurate, localized predictions for fluid phase behavior studies by utilizing adjacent mature samples.

The core limitation of the Phase Kinetics (PK) method lies in its reliance on immature shale samples as the starting point. Pyrolysis simulations of the complete maturity sequence result in cumulative fluids with an underestimated gas–oil ratio (GOR), making the method unsuitable for unconventional reservoirs like the Eagle Ford Shale. Addressing this, the shale-specific PhaseSnapShot (PS) method directly simulates the "instantaneously generated fluid composition during the transition from the reference well's maturity to the target well's maturity", as opposed to the "cumulative fluids" derived from immature samples in the PK approach. This ensures the simulation logic aligns perfectly with the "instantaneous generation" accumulation mechanism inherent to shales, thereby resolving the prediction bias of the PK method. This bias stems from the higher proportion of heavy components in its modeled cumulative fluids compared to the actual instantaneous fluids present in shales.

The conceptual model of the PK method focuses on the gas generation process from a single kerogen source and does not fully account for the critical influences of "kerogen-bitumen interactions" and "fluid retention" within the low-permeability shale matrix, leading to insufficient accuracy in its phase behavior predictions for shales. To address this limitation, the PS method optimizes the conceptual model by incorporating two shale-specific controlling mechanisms: Firstly, a dual reactive component synergistic gas generation mechanism, clarifying that shale fluids originate from both "gas generation within the low-permeability matrix by an intimate kerogen in situ bitumen mixture (KB)" and "separate gas generation from free bitumen (B) in the inorganic matrix", with KB interactions significantly enhancing gas generation efficiency. Secondly, consideration of C_7^+ fluid retention, quantified in the model based on measured data from the Eagle Ford Shale showing Oil Saturation Index (OSI) values near 100 mg HC/g TOC over the maturity range of 440–475 °C. This improvement enables the model to accurately replicate the phase control process in shales characterized by "retention of heavy components and generation of light gases", effectively resolving the prediction deviations of the PK method caused by its neglect of shale matrix properties.

2.3. Implications for In Situ Conversion Studies

Based on extensive pyrolysis experiments, numerical simulations, and practical validation, the PK and PS methods have systematically summarized the evolutionary patterns, key parameter changes, and controlling mechanisms of petroleum fluid phase envelopes under varying thermal maturity conditions. This body of work provides valuable guidance for studying the fluid phase behavior changes during in situ conversion heating processes. At low maturity stages, the phase envelope exhibits a wide and flat shape. As maturity increases, the maximum critical pressure rises while the maximum critical temperature decreases, causing the phase envelope to gradually transition into a taller and narrower shape. With further increases in maturity, the height of the phase envelope decreases again, presenting a narrow profile where the saturation pressure tends to stabilize (Figure 2).

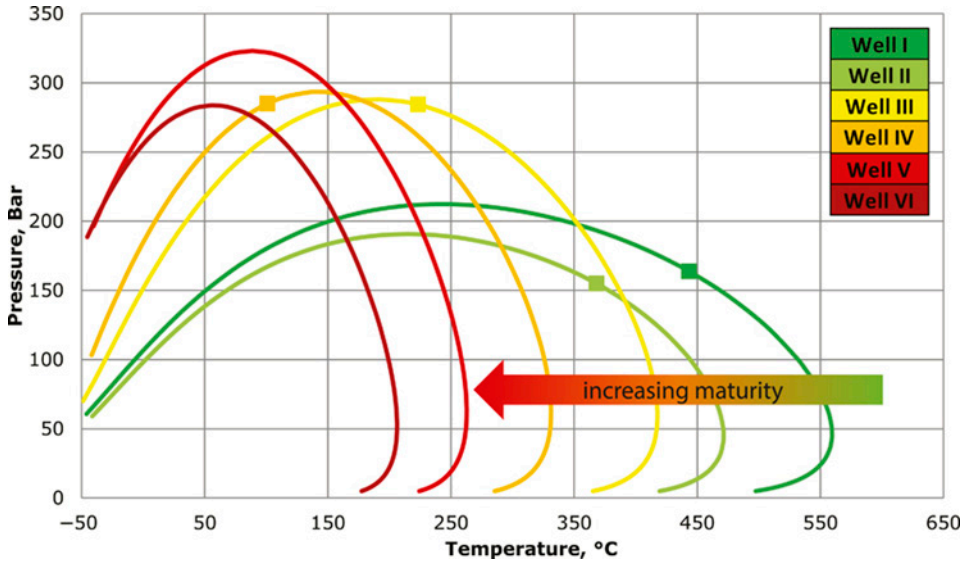


Figure 2. Phase envelopes of unconventional petroleum fluids with increasing maturity from the Eagle Ford Shale (modified from Kuske et al., 2017) [49].

The PK and PS models are designed for high-temperature, high-pressure formations with effective confinement. Therefore, parameters like the oil component distribution and

GOR in the actual reservoir show a high degree of consistency with predictions from closed-system pyrolysis experiments conducted on source rocks [50]. However, the target for in situ conversion technology for shale oil is organic-rich shale reservoirs at burial depths of 300–3000 m. While the heating conditions involve high temperature and pressure, the reservoir confinement is often relatively poor. The entire heating process constitutes a dynamic cycle of "generation and expulsion". During this process, especially in the early stages of thermal evolution, the generated oil and gas (particularly gases) are continuously expelled from the system. Therefore, the closed-system pyrolysis simulation experiments used in the PK and PS methods are not suitable for simulating pyrolysis under in situ conversion conditions. Other types of pyrolysis experiments need to be selected.

Secondly, during the in situ conversion process of shale oil, pyrolysis experiments conducted under artificial heating conditions more directly simulate the dynamic "generation-expulsion" process. The gas composition and GOR of the pyrolysis products from such experiments more closely resemble the characteristics of the actual produced fluids under this specific technological condition. Thus, for simulation experiments studying the fluid phase behavior during in situ conversion, there is no need to introduce additional gas composition corrections based on natural maturation systems. The experimental composition obtained can be considered a direct representation of the fluid phase behavior during in situ conversion.

3. Results

This section presents a systematic review, detailing the literature selection process related to the topic, the characteristics of the included studies, and the key findings of the research.

3.1. Study Selection

Our systematic search identified a total of 113 articles, 72 of which were excluded during the title and abstract screening phase. Ultimately, 37 articles proceeded to the full-text assessment stage. After evaluation, two articles met the inclusion criteria and were included in this review (Figure 3).

3.2. Study Characteristics

All articles included in this systematic review are introductory papers related to phase prediction methods based on hydrocarbon generation thermal simulation experiments. However, there is a scarcity of systematically reviewed literature in this field, so only two articles were included in the study. Both articles comprehensively elaborate on the methodological workflows of phase prediction based on immature or low-maturity samples, as well as the designed experiments and technical descriptions. We have organized the included studies according to their main research objectives, experimental types, and involved equations (Table 2).

Table 2. Main characteristics of the studies included in the systematic review.

Study	Reservoir Type	Hydrocarbon Generation Thermal Simulation Technology	Pyrolysis Technology Equation of State	Equation of State	Phase Behavior Simulation Technology
Di Primio et al., 2006 [31]	Conventional and Shale	Rock-Eval and MSSV	Py-GC	Not Specified	PVTsim
Kuske et al., 2019 [49]	Shale (Eagle Ford)	MSSV	Py-GC	Peng–Robinson Equation	PVTsim

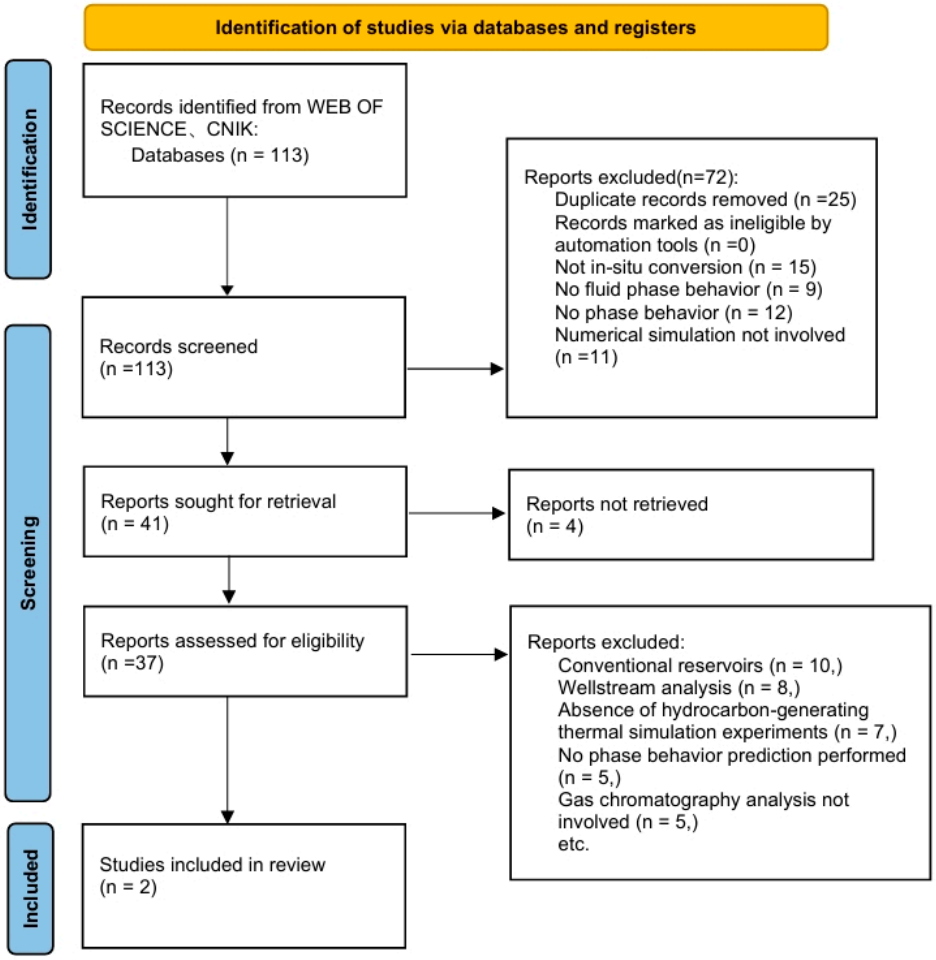


Figure 3. Flow diagram presenting the study selection process along with the number of included and excluded papers.

4. Selection and Application of Hydrocarbon Generation Thermal Simulation Experiments

The assessment of hydrocarbon generation potential and quantitative resource evaluation of source rocks is one of the core scientific issues in petroleum geology research. Hydrocarbon generation pyrolysis experimentation, as a key technology widely used in this field, serves as an important approach for predicting the hydrocarbon generation potential and evaluating the resources of source rocks [51]. To reveal different hydrocarbon generation processes of organic matter, the experimental samples, apparatus, and conditions for pyrolysis experimentation must be systematically designed and selected according to the specific experimental objectives [52].

4.1. Selection of Hydrocarbon Generation Thermal Simulation Experiments

The selection of samples for hydrocarbon generation pyrolysis experimentation is a decisive factor for reconstructing the geological evolution process from experimental results. Laboratory samples are generally divided into two major categories: standard compounds and geological samples. Standard compounds, such as n-alkanes and methylated aromatic compounds, are typically used to study and simulate the high-temperature secondary cracking process of hydrocarbons to generate gas or the mechanism of carbon isotope fractionation [53]. Geological samples, such as modern sediments, different types of source rocks and their extracts, kerogen, crude oil, and bitumen, can reveal different hydrocarbon generation processes of organic matter. For simulations aimed at reproducing

natural geological processes, whole rock samples, which completely retain the symbiotic relationship between organic matter and inorganic minerals, best represent the natural composition of source rocks and are the ideal choice for simulating hydrocarbon generation, expulsion, and organic–inorganic interactions within the formation [52].

The selection of experimental apparatus for hydrocarbon generation pyrolysis is crucial for reflecting differences in basin evolution processes and formation conditions. Based on the confinement of the system, experimental apparatus can be classified into open, closed, semi-open and semi-closed systems. Representative open systems, such as the Rock-Eval [54] and pyrolysis gas chromatography (Py-GC) [55], operate under a flowing inert carrier gas atmosphere. Pyrolysis products are immediately carried away from the reaction zone by the carrier gas and directly introduced into the analysis system. This offers advantages such as cost-effectiveness, high efficiency, real-time analysis, and effective avoidance of secondary cracking reactions of the products. It is suitable for studying primary cracking mechanisms of kerogen and obtaining hydrocarbon generation kinetic parameters [56,57]. However, this system has certain differences compared to real geological conditions.

Closed systems, represented by autoclaves, gold tube confined systems, and micro-sealed vessels (MSSV) [58,59], involve placing samples in sealed reaction vessels for thermal evolution. They allow precise control of temperature and fluid pressure and support experiments involving water. By effectively retaining pyrolysis products, they provide ideal experimental conditions for studying secondary cracking processes of crude oil and heavy hydrocarbon gases, natural gas generation mechanisms at high maturity stages, and the maximum gas generation potential of source rocks [60,61].

Semi-closed systems, characterized by generation accompanied by limited expulsion driven by the volume expansion of pyrolysis products, can simulate hydrocarbon generation and expulsion processes under conditions of overburden rock pressure [62]. Thus, semi-open pyrolysis systems more closely approximate actual geological conditions and are particularly suitable for isothermal simulation studies on whole rock samples. However, they are not suitable for continuous hydrocarbon generation simulation of source rocks. Furthermore, if the products are liquid hydrocarbons, they may not be expelled promptly due to the limited internal pressure buildup within the system [63].

4.2. Application of Hydrocarbon Generation Thermal Simulation Experiments

The conditions used in hydrocarbon generation pyrolysis experiments are critical factors that influence the processes of hydrocarbon generation and evolution of organic matter. The heating methods employed in simulation experiments are generally divided into two types: isothermal heating and programmed temperature heating. The final temperature settings for both methods are similar, typically ranging from 300 °C to 600 °C [52]. Temperatures set too low or too high would yield results significantly deviating from actual hydrocarbon generation processes. The heating rate in programmed temperature heating also affects the hydrocarbon generation evolution. Different heating rates (rapid vs. slow) significantly influence the conversion degree of organic matter in source rocks and the resulting products [64,65]. The pressure settings in simulation experiments also impact the conversion degree and products of organic matter. At different thermal evolution stages, fluid pressure exerts varying effects on the thermal evolution and hydrocarbon generation processes of organic matter. Increasing pressure at low temperatures promotes the generation of gaseous hydrocarbons, whereas at high temperatures, it conversely inhibits their production [66,67].

In shale systems, hydrocarbon generation does not occur in an absolutely confined or completely open extreme environment. Instead, it is a process of periodic hydrocarbon

expulsion jointly controlled by the rock's mechanical properties and the dynamic equilibrium between hydrocarbon generation, overpressure and pore fluid pressure. A semi-open and semi-closed pyrolysis system is designed to allow part of the generated fluids to be expelled under pressure-driven forces while retaining another portion within the source rock pores and organic matter. This simulates both primary migration and retention effects, thereby more realistically reflecting the evolution of fluid phase behavior during in situ conversion.

To better simulate the heating process of subsurface in situ conversion and replicate the actual dynamic cycle of "confined generation–accumulation–expulsion–re-confined generation", hydrocarbon generation thermal simulation experiments employing a semi-open and semi-closed system should be selected (Figure 4). The pyrolysis products include expelled gases and liquids, as well as oil retained within the solid residue. The expelled fluids are collected in real-time using collection tubes, subsequently rinsed, filtered, and weighed using a dichloromethane solution. Gases are collected using gas bags and then quantitatively analyzed via gas chromatography. The retained oil is extracted and weighed using a dichloromethane solution after the experiment concludes and the reaction vessel is opened.

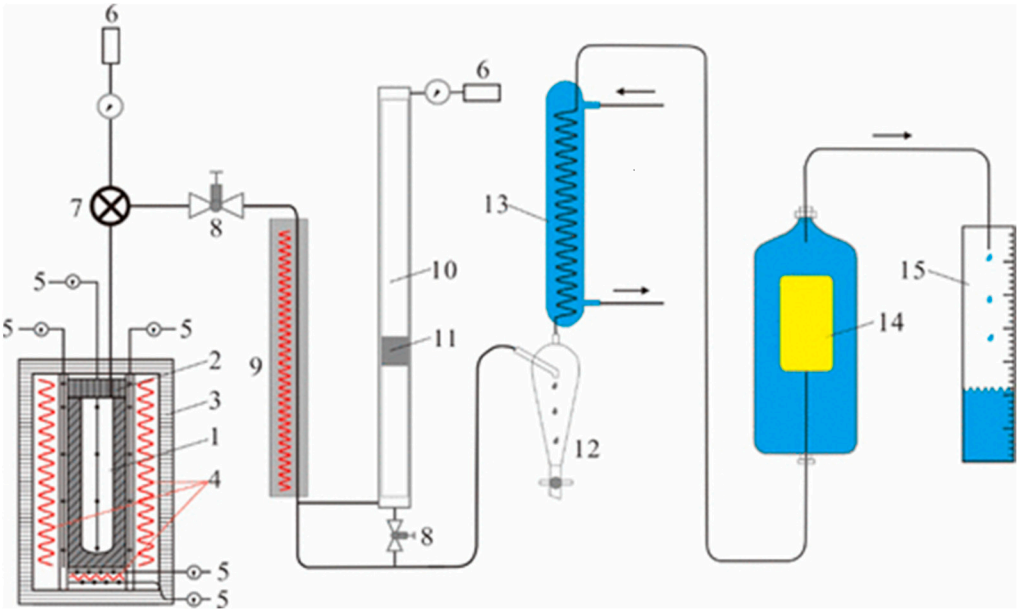


Figure 4. Semi-open and semi-closed system schematic diagram of the pyrolysis device [68]: (1) autoclave; (2) sealing cover; (3) outer cover; (4) electric heater; (5) thermocouple; (6) pressure gauge; (7) three-way valve controlled by solenoid valve; (8) needle valve; (9) heater; (10) synchronous motor; (11) floating piston; (12) liquid collector; (13) condenser; (14) gas bag; (15) measuring cylinder.

It is important to note that system pressure is a key factor governing expulsion behavior and product composition. Higher pressures inhibit fluid expulsion, prolonging its residence time at elevated temperatures. This promotes the secondary cracking of retained oil, leading to an increased proportion of gases and light components. To systematically elucidate the effects of temperature, pressure, and time on the phase behavior of in situ conversion fluids, the experimental design should encompass multivariate controls. This includes investigating the influence of different heating rates at a fixed final temperature, setting a series of final temperature points at the same heating rate, and further conducting comparative experiments under different pressure thresholds. Such a design facilitates the establishment of response relationships among temperature, pressure, and product com-

position, providing reliable experimental constraints and validation data for subsequent phase behavior simulation using equations of state.

However, the pyrolysis experimental conditions in semi-open and semi-closed systems still differ from actual geological conditions. The heating rates used in experiments are significantly faster than the natural geological heating rates, which may introduce deviations from the true kinetics of hydrocarbon generation and expulsion. Secondly, experiments typically employ homogenized, crushed samples, whereas actual source rocks exhibit multi-scale heterogeneity, leading to substantial differences in the pyrolysis process compared to that of uniformly ground samples. Furthermore, experiments apply a constant expulsion pressure, while the actual subsurface pressure field is dynamic and variable. These discrepancies collectively impact the accuracy of simulating the organic matter's hydrocarbon generation and expulsion processes.

5. Selection and Application of Analytical Techniques for Pyrolysis Products

When performing phase simulations using PVT modeling software, the fundamental input consists of a detailed description of the fluid composition, including the molar contents of C_1–C_5 alkanes and their isomers, as well as liquid-phase components typically divided into at least two groups [31]. In other words, the compositional structure and relative abundance of pyrolysis products are the fundamental determinants of phase simulation outcomes—particularly the proportions and configuration of gaseous components, which exert a significant influence on phase behavior characteristics [49].

Thermal simulation experiments typically yield three categories of products: oil, gas, and pyrolysis residues. The gaseous and liquid hydrocarbon products are commonly analyzed qualitatively and quantitatively using gas chromatography (GC) or gas chromatography–mass spectrometry (GC–MS) [69]. Gases generated during in situ heating not only include C_1–C_5 alkanes and their isomers but also non-hydrocarbon gases such as CO_2, H_2S, and N_2, all of which require precise qualitative and quantitative determination. In laboratory practice, the Agilent 7890 N gas chromatograph is widely used for analyzing gaseous products. Equipped with a thermal conductivity detector (TCD), it can detect all gas components with differing thermal conductivities in the carrier gas, providing a broad detection range that covers H_2, O_2, N_2, CO_2, H_2S, and C_1–C_5 hydrocarbons. The flame ionization detector (FID) offers exceptionally high sensitivity for hydrocarbon gases, enabling precise quantification of C_1–C_5 components, though it cannot detect sulfur-bearing compounds [70].

Gas chromatography–mass spectrometry (GC–MS) is a critical analytical technique in modern chemistry, enabling simultaneous separation and structural identification of complex mixtures. By interfacing GC's efficient separation with MS's molecular identification capability, GC–MS allows precise qualitative and quantitative characterization of complex organic mixtures [71,72]. However, since GC separation relies on volatility and thermal stability, high-boiling-point compounds such as heavy oils and bitumens tend to remain in the chromatographic column, leading to incomplete separation and reduced analytical accuracy.

Consequently, GC–MS is best suited for analyzing the carbon number distribution and compositional groupings of middle distillate hydrocarbons, whereas for heavy oils and high-molecular-weight compounds, higher-resolution mass spectrometry techniques [73] such as Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT–ICR MS) or Field Ionization Time-of-Flight Mass Spectrometry (FI–TOFMS) are required to achieve comprehensive molecular-level characterization [74,75].

For the products of semi-open and semi-closed thermal simulation experiments, gaseous and liquid fractions are collected separately; accordingly, gas chromatography-mass spectrometry (GC-MS) analyses are performed independently for these two phases. For gaseous fraction analysis, a suite of standard gas mixtures is employed to construct a quantitative calibration curve that correlates retention time and chromatographic response with each target component. Subsequently, the target gas sample is injected into the GC-MS system under identical analytical parameters. Chromatographic peaks are qualitatively identified via matching retention times to those reference standards, thereby confirming the presence of specific compounds (such as methane, ethane). Finally, the absolute concentration (or content) of each component is quantified using the pre-constructed calibration curve, with calculations anchored to the response intensity of each corresponding chromatographic peak [76].

For liquid oil fractions, the sample is first subjected to pretreatment to isolate saturated hydrocarbon and aromatic hydrocarbon sub-fractions. Using the chromatographic retention times of an n-alkane standard series as a reference, the sample chromatogram is initially segmented into carbon number ranges, ordered by increasing boiling point [77]. Subsequently, corrections are implemented to account for elevated boiling points of aromatic hydrocarbons (attributed to their polarity) and for highly isomerized alkanes. Finally, by integrating mass spectrometric identification data for compound classes within each carbon number range, the mass percentages of distinct hydrocarbon types across different carbon numbers are quantified using a standardized computational model [78].

In summary, gas chromatography and its coupled techniques provide an efficient means of identifying various gases and light hydrocarbons generated during in situ conversion processes, while high-resolution mass spectrometry serves as a powerful complement for characterizing heavy distillate fractions. The combination of both methods enables comprehensive elucidation of fluid compositional evolution during pyrolysis.

6. Selection of Equation of State (EOS)

The essence of an equation of state (EOS) is a mathematical model capable of describing the relationship between pressure, volume, and temperature (P–V–T) of a fluid. Phase behavior numerical simulation using PVT software involves predicting key phase parameters—such as the phase envelope, saturation pressure, vapor–liquid equilibrium constants, phase densities, viscosities, and enthalpy—from a given set of fluid compositions [31].

The choice of EOS is the key factor determining the accuracy of model predictions. Reference to the PS and PK methods, the Peng–Robinson (PR) equation [79] and the Soave–Redlich–Kwong (SRK) equation [80] are currently the two most widely applied cubic equations of state. The SRK equation, as an important modification of the Redlich–Kwong (RK) equation [81], features a relatively simple form and high computational efficiency. However, it performs poorly in predicting liquid-phase volumetric properties, generally underestimating liquid densities, with particularly significant deviations for larger-molecule hydrocarbons such as butane and heavier components.

To address the limitations of the SRK equation in predicting liquid-phase density, a new equation—the Peng–Robinson (PR) equation—was developed, maintaining simplicity while achieving greater predictive accuracy. The core improvement of the PR equation lies in modifying the attractive pressure term of the SRK equation, allowing for a more precise description of intermolecular attractive forces. As a result, the predicted critical compressibility factor (Zc) decreases from 0.333 in the SRK equation to 0.307 in the PR equation, which is closer to the range of most real fluids, especially hydrocarbons.

Therefore, in PVT phase simulation software, the PR equation is also frequently used for numerical simulations [82,83].

As a cubic equation of state, the binary interaction parameters (BIPs) in the Peng–Robinson (PR) equation serve as pivotal correction factors to ensure accurate predictions of the properties of real fluid mixtures, exerting a significant influence on the modeled phase behavior [84]. Among the substances that most critically affect BIPs in petroleum-related systems are non-hydrocarbon gases with small molecular dimensions yet distinctive intermolecular forces, such as carbon dioxide and hydrogen sulfide. Notably, substantial amounts of CO_2 and H_2S are generated during the in situ conversion heating process. Hence, particular and meticulous attention must be paid to these components when applying the PR equation of state for numerical phase behavior simulations.

7. Conclusions

In the study of the phase behavior evolution of fluids during in situ conversion, existing methods that predict hydrocarbon phase behavior based on low-maturity source rocks of different organic facies are improved in consideration of the specific characteristics of in situ conversion. The semi-open and semi-closed system can simulate the intermittent hydrocarbon expulsion process caused by pressure buildup and release within subsurface shale formations. This is more consistent with the geological reality that fluid production during in situ conversion is not continuous or stable but accompanied by pressure fluctuations, and thus better reflects the kinetics of hydrocarbon expulsion compared with a completely closed system.

The semi-open and semi-closed thermal simulation system is capable of simulating the intermittent hydrocarbon expulsion process in subsurface shale systems caused by pressure accumulation and release. This aligns more closely with the geological reality of in situ conversion, where fluid production is not continuous and stable but accompanied by pressure fluctuations. Consequently, it provides a more realistic simulation of the intermittent expulsion driven by pressure build-up and release in underground shale compared to a fully confined system. The hydrocarbons expelled by this system represent the fraction capable of "migrating" under the experimental temperature and pressure conditions, which corresponds precisely to the effective product targeted for recovery by in situ conversion technology.

Gas chromatography–mass spectrometry (GC–MS) is currently the most widely applicable analytical technique for product characterization and serves as the gold standard for the qualitative analysis of complex organic mixtures. It provides a highly reliable molecular compositional dataset essential for subsequent phase behavior simulations. The Peng–Robinson (PR) equation of state, as one of the most widely used equations in the oil and gas industry, offers sufficient reliability and computational efficiency for vapor-liquid equilibrium and saturation pressure calculations in conventional hydrocarbon systems, ensuring accurate prediction from experimental data to phase behavior. Therefore, by analyzing the products of intermittent expulsion from semi-open/semi-confined thermal simulation experiments using GC–MS and integrating this with numerical simulation based on the PR equation, the results can directly reflect the phase segregation that occurs during the expulsion process.

By using a semi-open and semi-closed thermal simulation system to model the hydrocarbon generation and expulsion process during in situ conversion, applying GC–MS for qualitative and quantitative analysis of the products, and finally performing phase behavior simulation with numerical software and the Peng–Robinson (PR) equation of state, this combined approach can effectively reveal the evolution of fluid composition with maturity. It enables qualitative assessment of the effects of pressure, temperature, and heating

rate on expulsion efficiency and product characteristics, and provides trend prediction and mechanistic analysis of fluid phase behavior during in situ conversion production. Subsequently, comparing and calibrating the phase behavior predictions obtained from this methodology (such as GOR, saturation pressure, phase envelopes) against the produced fluid data from large-scale physical simulation apparatuses or the measured production data from ICP field pilot tests will be crucial for validating the predictive accuracy and reliability of the method.

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