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Numerical simulation of oil shale retorting optimization under in situ microwave heating considering electromagnetics, heat transfer, and chemical reactions coupling

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Supplementary Materials

Oil shale constitutes an important proportion of unconventional resources in China, and its efficient exploitation helps alleviate the Chinese oil shortage situation. Microwave heating is a promising method to in situ exploit oil shale reservoirs. In this study, a novel pseudo three-dimensional electromagnetic-thermal-chemical model was developed and implemented based on the finite element method to investigate the retorting performance of oil shale reservoir under microwave heating. To precisely simulate the heating process, oil shale properties including density, specific heat, thermal conductivity, dielectric constant, loss factor, and porosity were considered as temperature-dependent. The effects of microwave power, antenna number, and antenna position were analyzed to reveal the retorting mechanism of microwave heating. Since the model is well-established for oil shale in situ retorting under microwave heating, the result can guide the optimization of microwave heating parameters. Governing equations of this model was as follows.

1. Governing equations

Although Figure 1 already shows the multiple physical and chemical processes in this model, it is necessary to show the specific equations and their relationship in the supporting information.

Electromagnetics:

Due to the high frequency of the electromagnetic field, it should be described using the wave equation when microwave propagates through the formation. The time-harmonic electromagnetic field distribution within oil shale is obtained by the Maxwell's equations (Eqs. S1-S5). The heat source from electromagnetic excitation is calculated by Eq. S7. The temperature from energy conservation is coupled with electromagnetic physics by setting the temperature-dependent characteristics of oil shale reservoir.

$$\nabla \times \boldsymbol{H} = -\frac{\partial \boldsymbol{D}}{\partial t} + \boldsymbol{J} \tag{S1}$$

$$\nabla \times \boldsymbol{E} = -\frac{\partial \boldsymbol{B}}{\partial t} \tag{S2}$$

$$\nabla \cdot \boldsymbol{D} = \rho_{ec} \tag{S3}$$

$$\nabla \cdot \boldsymbol{B} = 0 \tag{S4}$$

where **E** denotes the electric field intensity (V/m), **B** denotes the magnetic flux density (Wb/m^2), **H** denotes the magnetic field intensity (A/m), **D** denotes the electric displacement or electric flux density (A/m^2), **J** denotes the current density (A/m^2), and ρ_{ec} denotes the electric charge density (C/m^3).

To solve the time-harmonic electromagnetic field distributions, the frequency domain approach can be used to simplify Maxwell's equations to the Helmholtz vector equation:

$$\nabla \times \mu_r^{-1}(\nabla \times \boldsymbol{E}) - \mathrm{k}_0^2(\varepsilon_r - \frac{j\sigma}{\omega\varepsilon_0})\boldsymbol{E} = 0 \tag{S5}$$

The tube is assumed as the perfect electric conductor for setting the boundary condition (Eq. S6).

$$n \times E = 0 \tag{S6}$$

During microwave heating, the electromagnetic losses Q_e (W/m^3) can be regarded as a heat source in the heat transfer part of the model. Consequently, the microwave apparatus is regard as the electromagnetic heat source. It is provided by (Eq. S7)

$$Q_e = \frac{1}{2}\mathrm{Re}(J \cdot E^*) + \frac{1}{2}\mathrm{Re}(i\omega B \cdot H^*) \tag{S7}$$

Energy conservation equation:

The energy conservation equation (Eqs. S8-S10) is applied to describe the temperature distribution within oil shale reservoir, which includes the energy convection by momentum conservation, the heat conduction by temperature gradient, the heat source from electromagnetic excitation (Eq. S7), and the exothermic reactions from kerogen decomposition (Eq. S20).

$$\left(\rho C_P\right)_{\mathrm{eff}} \frac{\partial T}{\partial t} + \nabla \cdot q = Q \tag{S8}$$

$$q = -k_{\mathrm{eff}} \nabla T \tag{S9}$$

$$Q = Q_e + Q_c \tag{S10}$$

According to heat conduction, the effective thermal conductivity of oil shale is calculated based on the volume fractions of the matrix and pore volume (Eq. S11).

$$k_{\mathrm{eff}} = \theta_{\mathrm{p}} k_{\mathrm{p}} + \left(1 - \theta_{\mathrm{p}}\right) k_f \tag{S11}$$

The walls in the temperature transfer domain of the oil shale reservoir are considered as heat insulation conditions (Eq. S12). The dielectric constant of oil shale changes with temperature; the coupling of electromagnetics and energy conservation is implemented.

$$-\mathrm{n} \cdot q = 0 \tag{S12}$$

Mass conservation equation:

In the oil shale reservoir, the mass transfer depends on the convection, diffusion, and chemical reactions (Eqs. S13-S15). The diffusion of the products is controlled by the concentration gradient and tortuosity of porous media (Eq. S16). The convection of the products is determined by the momentum conservation. The perforation location is taken as the outlet of the production well.

Chemical components from kerogen decomposition are transported through porous media via diffusion. The mass conservation equation for one chemical component i is applied to solve the concentration distribution of each chemical:

$$\frac{\partial(\varepsilon_p c_i)}{\partial t} + \nabla \cdot \boldsymbol{J}_i = R_i \tag{S13}$$

where ε_p denotes the porosity of oil shale, which equals ($1-\theta_p$), R_i represents the mass source due to the chemical reaction (mol/(m^3·s)), and $\mathbf{J}_i$ denotes the mass flux relative to the mass-averaged velocity (mol/(m^2·s)). In this model, $\mathbf{J}_i$ determines the diffusive flux vector.

$$\boldsymbol{J}_i = -D_{\mathrm{e,i}} \nabla c_{\mathrm{i}} \tag{S14}$$

where $D_{e,i}$ denotes the effective diffusion coefficient of component i in porous media (m^2/s). It depends on the structure of the porous media and the phase involved:

$$D_{\mathrm{e,i}} = \frac{\varepsilon_p}{\tau_{F,i}} D_{F,i} \tag{S15}$$

where $D_{F,i}$ denotes the single-phase coefficient for component i (m^2/s), and $\tau_{F,i}$ is the tortuosity of the porous media based on the Millington and Quirk model:

$$\tau_L = \varepsilon_{\mathrm{p}}^{-1/3} \tag{S16}$$

The outlet boundary condition for the mass transport field is provided by:

$$-n \cdot D_i \nabla c_i = 0 \tag{S17}$$

Chemical reactions:

Kerogen decomposition and the secondary oil cracking are considered throughout oil shale reservoir once the formation temperature reaches the pyrolysis temperature. All the chemical reactions are obtained by the first order rate law and Arrhenius equation (Eqs. S18-S19). The heat from exothermic reaction is acquired by the enthalpy from all the chemical reactions (Eq. S20).

Chemical reactions occur based on the reaction rate. We compute the reaction rates of the thermal decomposition of kerogen in oil shale samples by using the first-order rate law because all the chemical reactions that we consider are first-order rate reactions. The reaction rate equation is as follows:

$$r_j = k_j^f \prod_{i \in react} c_i^{-v_{ij}} \tag{S18}$$

where r_j is the reaction rate (mol/(m$^3 \cdot$ s)), subscript j represents the reaction, and i denotes the component, k_j^f denotes the forward rate constant due to the irreversible decomposition of kerogen (mol/(m$^3 \cdot$ s)). The concentration of component i is denoted as c_i (mol/m^3). The stoichiometric coefficient is v_{ij}, and is defined to be negative for reactants and positive for products.

In addition to the concentration dependence, the temperature dependence is simulated by using the Arrhenius expressions for the rate constants:

$$k_j = A_j \exp(-\frac{E}{R_g T}) \tag{S19}$$

where A_j is the frequency factor (1/s), E_j is the activation energy of reaction j (J/mol), and R_g is the gas constant (8.314 J/(mol $\cdot$ K)).

The heat Qc generated from complex chemical reactions is defined as:

$$Q_c = -\sum_j k_j H_j \quad \text{(S20)}$$

There are complex chemical reactions of kerogen decomposition when oil shale is subjected to the microwave field. Table 1 summaries each reaction's kinetic parameters [26]. It can be seen that kerogen is first converted to heavy oil and light oil. Simultaneously, the cracking of oil products also occurs at high temperature, forming lighter fluid products and solid coke.

The relative permittivity ε′ and the relative loss factor ε″ represent the microwave absorption capacity of specific material. The ε′ and the relative ε″ of oil shale are shown in Figure S1 [27]. In addition, the ε′ of shale is 3 and the ε″ of shale is 0.2 [28,29].

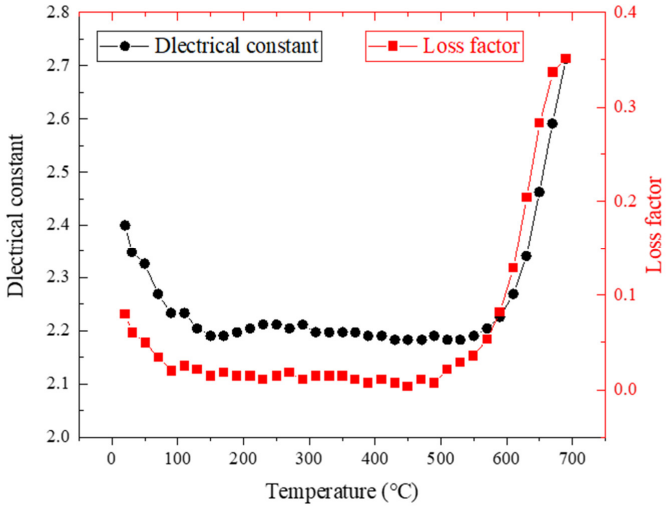

Figure S1. The relative permittivity and relative loss factor of oil shale at different temperature.

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