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# A stochastic kinetic study of preparing fatty acid from rapeseed oil via subcritical hydrolysis <sup>☆</sup>

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## HIGHLIGHTS

- Theoretical support of kinetic model under high temperature and pressure is verified.
- A stochastic kinetics model under high pressure and temperature is described.
- Nonlinear features of reaction velocity constant and reaction order are determined.
- An optimized method for controlling the adding time of raw materials is obtained.

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## ABSTRACT

A kinetic model based on the elementary reaction velocity theory is useful for investigating the kinetic rules of chemical reactions under subcritical and supercritical conditions. This model can be used to determine the stochastic relations between the hydrolysis products and conversion time in subcritical water based on the molecular collision theory. First, hydrolysis reaction experiments using rapeseed oil were conducted, and the collected data were used to verify the effectiveness of this stochastic kinetic model. The results showed that the kurtosis of this model was 1.11922, skewness was  $-1.49277$  and mean error of the system was 0.81499, which was relatively small. Meanwhile, the adjustment coefficient ( $\text{Adj. } R^2$ ) was 0.98923, which indicated that this model is highly significant, that is, it can accurately depict the microscopic stochastic process of the rapeseed oil hydrolysis reaction. Furthermore, it verifies that the stochastic theory and molecular collision theory are feasible under subcritical conditions, which is a breakthrough in the field of the kinetic study of high-temperature and high-pressure reaction systems. Furthermore, the model reveals the changing rules of the reaction order and reaction velocity of the rapeseed oil hydrolysis reaction, which provides an important reference for parameter optimization of industrial reactor design.

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## 1. Introduction

New energy and new energy technologies are becoming a focus of research of many governments around the world. The energy crisis presents a new opportunity for the development and exploitation of renewable energy sources. Biomass energy has attracted wide attention due to its common, clean and renewable

properties [1]. Biodiesel is biodegradable and regenerative, which has allowed it to gain strong support from governments worldwide [2].

Currently, there has been significant research regarding the preparation methodology, techniques and reaction conditions of biodiesel by different oils [3,4]. Saka's [5] proposal of a supercritical method enjoys advantages, such as a low demand for raw materials, absence of a catalyst, short reaction time and high conversion efficiency, but its commercialization is restricted due to the growing input cost that results from the high temperature and high pressure required by the preparation process [6]. The use of subcritical water in the supercritical methanol method, i.e., the two-step method, is an improvement that is based on the supercritical method. It requires a lower temperature and pressure. However, study of the method preparation conditions and processing

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## Nomenclature

|                    |                                                                                                         |                                                      |                                                             |
|--------------------|---------------------------------------------------------------------------------------------------------|------------------------------------------------------|-------------------------------------------------------------|
| $X_i(t)$           | the number of molecules of the $i$ th substance at time $t$                                             | $n$                                                  | order of reaction                                           |
| $\dot{t}$          | the time of chemical reaction                                                                           | $k_1$                                                | ratio of reaction velocity constant                         |
| $(\tau, j)$        | Random number couple                                                                                    | $D$                                                  | mean square deviation, 1/s                                  |
| $m, \xi$           | the state of molecules                                                                                  | $c_{AO}$                                             | initial concentration of solute of reaction solution, mol/L |
| $V$                | the scale of chemical reaction system                                                                   | $x(t)$                                               | stochastic process                                          |
| $P_m(t)$           | the probability of the system at state $m$ and $t$ moment                                               | $P(w, t)$                                            | probability density function                                |
| $\mathbf{A}$       | transition rate matrix                                                                                  | $k_2$                                                | represents the ratio of $k_1$ and $c_{AO}$                  |
| $P(\tau, j X', t)$ | the probability of next reaction at when the number of molecules is $X'$ at $(t + \tau, t + \tau + dt)$ | $P(x_1, t_1; x_2, t_2, \dots, x_n, t_n)$             | $n$ -order joint probability density function               |
| $X'$               | the number of molecules                                                                                 | $P(x_2, t_2; \dots; x_n, t_n   x_1, t_1)P(x_1, t_1)$ | conditional probability density function                    |
| $K$                | the number of chemical species                                                                          | $P(w_1, t_1)$                                        | a first-order probability density function                  |
| $a_0(X')$          | the sum of trend functions of all reactions at that moment                                              | $\eta, S$                                            | transformed variables                                       |
| $S_A$              | saponification value                                                                                    | $P(x_0, t_0)$                                        | original first-order probability density function           |
| $C_1$              | theoretical acid value of fatty acid, mgKOH/g <sub>oil</sub>                                            | $P(x,  x_0, t_0)$                                    | transition probability                                      |
| $C_2$              | actual acid value of hydrolysis product, mgKOH/g <sub>oil</sub>                                         | $\alpha_1, \alpha_2$                                 | moment parameters                                           |
| $C_0$              | original acid value of rapeseed oil, gKOH/g <sub>oil</sub>                                              | $\alpha_n(x, t)$                                     | moment of increment $x(t + \Delta t) - x(t)$                |
| $C$                | concentration of KOH-alcohol standard solution, mol/L                                                   | $f(x, t)$                                            | a deterministic function                                    |
| $V$                | volume of KOH-alcohol standard solution used in the titration, ml                                       | $H(t)$                                               | Wiener process                                              |
| $m$                | sample mass of the hydrolysis product, g                                                                | $\varphi(x, t)$                                      | represent the derivative of $x(t)$                          |
| $x$                | change of rapeseed oil conversion rate, %                                                               | $T$                                                  | reaction temperature                                        |
| $t$                | converting time, min                                                                                    | $P^*$                                                | reaction pressure                                           |
|                    |                                                                                                         | $O^*$                                                | oil-water ratio                                             |

parameters has currently stagnated [7,8], especially with regard to the parameters of reaction pressure, which have large effects on the design and optimization of reactors. At present, most kinetic studies use the elementary reaction velocity theory to predict kinetic rules of reactions [9–11]. However, this theory does not consider pressure [12]. In the preparatory process for the two-step method, the reaction pressure is the vital condition and a key parameter [13]. Therefore, there is still controversy regarding whether the elementary reaction velocity theory is suitable for use in the two-step method in academia [14,15]. Novel theories are needed.

The stochastic kinetic model is based on molecular collision theory, which can directly analyse the relation between targeted products and conversion time [16,17] and overcome the inability of the elementary reaction velocity theory to deal with pressure [18–20]. Thus, this paper adopts a stochastic kinetic model to explore the relation between targeted hydrolysis products and the conversion time in subcritical water and to analyse the stochastic kinetics of the hydrolysis reaction, which offers evidence for the optimized design of industrial reactors, thereby improving biodiesel production, which is of great significance to facilitate the commercialization of biodiesel.

## 2. Research questions and experimental design

### 2.1. Research question

A chemical reaction kinetics study usually refers to the study of the reaction time, reaction conditions and detailed procedures of an entire reaction [21,22]. From a dynamic perspective, it is the process of exploring the reaction velocity and mechanism from the macro phenomenological to micro molecular levels [23,24].

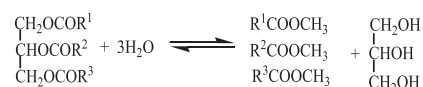
In recent years, with chemical research extending into life systems and nanosystems, research on the stochastic rules of mesoscopic chemical systems has become an increasingly important topic of wide concern [25]. According to the traditional macro reaction stochastic theory, the evolutionary rule of the system status  $X_i(\dot{t})$  can be described by

$$\frac{dX_i(t)}{dt} = f_i(X_1(\dot{t}), \dots, X_N(\dot{t})), (i = 1, \dots, N) \quad (1)$$

where  $X_i(\dot{t})$  stands for the number of molecules of the  $i$  th substance at time  $\dot{t}$ .

When the scale of the chemical reaction system  $V$  decreases to the mesoscopic scale, its internal fluctuation grows strikingly [26]. At this moment,  $X(\dot{t}) \equiv (X_1(\dot{t}), \dots, X_N(\dot{t}))$  is the stochastic variable of discreteness and the macro determined equation is invalid [27].

Molecular collision theory states that when enough particles (molecules, or atoms, or ions) of the reactant hit each other, only a certain percentage of the collisions cause a noticeable or significant chemical change [28]. These successful changes are referred to as successful collisions [29]. The successful collisions have enough energy, also known as activation energy, at the moment of impact to break pre-existing bonds and form entirely new bonds [30]. This results in the products of the reaction. The rate of successful collisions at any point in time reflects the kinetics of the chemical reaction. From a mathematics perspective, the type of molecular collision process can be regarded as an abstract stochastic process [31]. In a reversible reaction, positive successful collisions refer to the generation of the targeted product; negative successful collisions refer to the synthesis of raw materials [32]. The rate difference between positive and negative successful collisions at the same moment is the production of the targeted product [33]. The hydrolysis reaction equation of rapeseed oil in sub-critical water is:



Judging from the equation, hydrolysis is reversible. Usually, a common first-order kinetic equation and second-order kinetic equation are incapable of analysing the stochasticity of the reaction [34]. Therefore, we adopted a stochastic kinetic model to

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