Study on digestion kinetics model of wood extractives from *Eucalyptus camaldulensis* biomass

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ABSTRACT

Eucalyptus camaldulensis is one of the most widely planted eucalypts in the world. However, rich extractives in E. camaldulensis wood leads to serious defects such as amount of pulping wastewater, lower bonding strength, bad finishing effect, and the wood extractives is considered as the key negative factors. Therefore, the leaching characteristics of wood extractives was studied by mathematical model according to fuzzy theory. Theresultsshowed thatthe kinetics of wood extractives were divided into three phases: the rapidly leaching stage, the slowly leaching stage, the equilibrium leaching stage. The reaction of wood extractives leaching from E. camaldulensis biomass could be considered as a first-order reaction. Theorder of reaction was 1.02, the activation energy ofreaction Ea=14549.86J/mol, and the pre-exponential factor A=20.48min^{-1}.

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KEYWORDS

Digestion kinetics model;
Wood extractives,
*Eucalyptus camaldulensis*biomas;
Fuzzy mathematical model.

INTRODUCTION

Eucalyptus is one of the world's three famous fast-growing species and the preferred fast-growing reforestation species in tropical and subtropical regions. And *Eucalyptus camaldulensis*, which is native to Australia, is an important species of *Eucalyptus*. It is commonly planted along many waterways in Australia. Because of its many advantagesincluding red wood, optimum density and beautiful texture, *E. camaldulensis*was introduced to the rest of the world besides Brazil, China and India.And *E. camaldulensis*wood has been widely used to produce paper, wooden floor, wood based panel, and so on. Now it is one of the most widely planted eucalypts in the world[1].

Wood extractives contained many types of natural organic compounds including polyphenols, resin acids, terpenes, esters, carbohydrates, etc[2]. There was rich extractives in*Eucalyptus camaldulensis* biomass. And the extractives was traditionally used inAboriginal folk medicine to treat a wide variety of ailments from cold and cough to wounds and fever[3]. However, *E. camaldulensis* wood extractives caused some processing defects, such as amount of pulping wastewater, easy-fall-off film in finishing process, and poor gluing effect[4,5]. And many researchers tried to eliminate the side effects of wood extractives[6]. But every molecule of wood extractives leached out at random[7,8], andit was difficult to clearly reveal the leaching characteristics. Therefore, the digestion kinetics characteristics of *Eucalyp-*

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tus camaldulensis wood extractives were analyzed and established by fuzzy mathematical model in order to fully utilizing resources and controling harm on wood processing.

MATERIALS AND METHODS

Materials

A 18-year-old Eucalyptus camaldulensis wood with the diameter of 20cm at 1.5-2m height from ground was collected from Zhuzhou Forest Farm of Central South University of Forestry and Technology, Hunan province, P.R.China. The sample chips with the dimension of 32-36 mm (width)×9-20mm (height)×0.3-0.4 mm (thickness) were chipped by the flaker (Model: BX484, Made in China). Theabove-mentioned chips were baked to absolutely dry under the conditions of vacuum degree of 0.01MPa at 55°C, then processed into 40 to 60 mesh wood powder, and finally stored in a desiccator for the subsequent experiments.

Benzene (chromatographicgrade), ultra pure water,ethanol (chromatographicgrade), and the filter papers and cottonextracted in the benzene/ethanol solution ($V_{ethanol}/V_{benzene}=2$) for 24h were prepared for the subsequent experiments.

Methods

Weighed 30 pieces of wood powders, each was about 5g (0.1mg accuracy) and finally parceled by using the quantitative filter paper and tied by using cotton thread, and signed. Extraction was carried out in 50ml benzene/ethanol solution by the Foss method for 3h, 6h, 9h and 12h under the condition of 70°C, 80°C and 90°C, respectively. Parallel sample number was 2.

RESULTS AND ANALYSIS

Leaching law of wood extractives

Wood powder was extracted by benzene/ethanol solution under 70°C, 80°C and 90°C, respectively. The leaching rate of wood extractives was showed in TABLE 1. The curves of leaching rate were showed in Figure 1.

The dissolution of extractives could be divided into three stages. The first stage was the rapidly leaching

stage of 0-8h. At this stagewith the greatest rate at the beginning, but the rate reduced gradually. The second stage was the slowly leaching stage of 8-20h where wood extractives leached out massively and the rate flattened out gradually. The third stage was the equilibrium leaching stage of more than 20h where wood extractives leaching gotequilibrium state.

TABLE 1 : The results of leaching rate

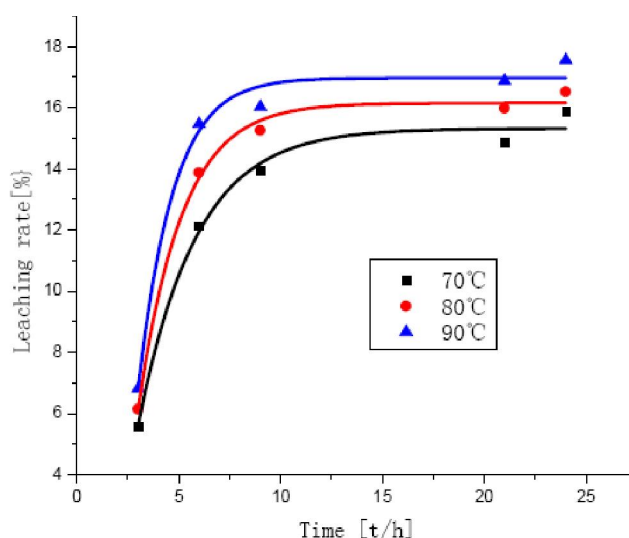| Extraction time [h]	Extraction temperature[°C]		
	70	80	90
3	5.59	6.14	6.82
6	12.13	13.87	15.47
9	13.95	15.26	16.03
21	14.86	15.98	16.88
24	15.87	16.52	17.56

Figure 1 : Dissolving profile of benzene/ethanol extractives

Dissolution kinetics of extractives

The research of dissolution kinetics of extractives was described from the following three aspects: reaction order, the reaction rate constant and the reaction activation energy. The leaching of wood extractives was the complex multiphase chemical reaction, which couldn't be expressed by regular equation. Some equations were used to obtain macroscopic kinetic equations when conducting analysis. The leaching of extractives met the quality function law in the condition of the large liquid ratio, and the concentration of retting can be regarded as a constant. So the formulation of dissolution kinetics could be simplified. Take the effect of various factors on the leaching of extractives into ac-

count, concluded by using the exponential form, equation was as follows:

$$-\frac{dE_t}{dt} = k \cdot (E - E_0)^\alpha \cdot C^\beta \qquad \text{(1)}$$

$-\dfrac{dE_t}{dt}$ —— dissolution rate of extractives; E_t—— content percent of extractives that can leach out (%),that is $E_t=E-E_0$; K—— dissolution rate constant; E—— residual quantity of extractives; E_0——*amount of* extractives that is difficult to extractin given conditions; C—— concentration of retting; α, β—— reaction order, constant; t—— reaction time

During the dipping process, hypothesis the concentration of retting C_A was constant. Equation (1)could be transformed into:

$$-\frac{dE_t}{dt} = k_0 \cdot E_t^\alpha$$

Determination of the reaction order

In order to get reaction rate, rate constant and activation energy, benzene/ethanol solution and alkaline solution were used to extract the wood powder at 70°C080°C and 90°C, respectively. According to the experimental results (TABLE 2), target constants could be gained. Amount of the extractives to absolutely dry wood powder at all time points were determined, the remnants E of extractives in wood powder was calculated, then the E_t could be evaluated.

TABLE 2 : The residual rate of wood extractives

Time	70°C		80°C		90°C	
[h]	E	E_t	E	E_t	E	Et
3	17.61	11.98	17.06	11.43	16.38	10.75
6	11.07	5.44	9.33	3.7	7.73	2.1
9	9.25	3.62	7.94	2.31	7.17	1.54
21	8.34	2.71	7.22	1.59	6.32	0.69
24	7.33	1.7	6.68	1.05	5.64	0.01

According to equation (1), reaction order was got by using differential method. Took logarithm to equation (1) on both sides:

$$\lg(-\frac{dE_t}{dt}) = \lg k_0 + \alpha \cdot \lg E_t \qquad \text{(2)}$$

Made a figure of $\lg(-\dfrac{dE_t}{dt}) - -\lg E_t$, then a straight

line could be got, the slope of which was the value of α, representing the reaction order. Take the experiment at 90°Cas an example. The concentration of extracts that could leach (E_t) and reaction rate $-\dfrac{dE_t}{dt}$ should be got first, then build a curve of E_t—t (As shown in Figure 3),
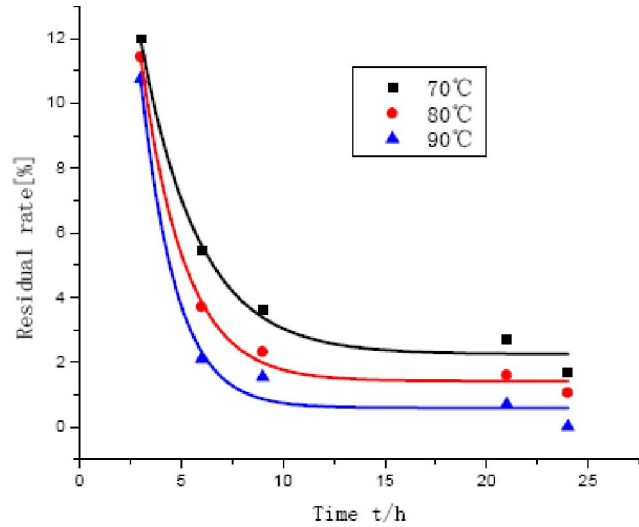

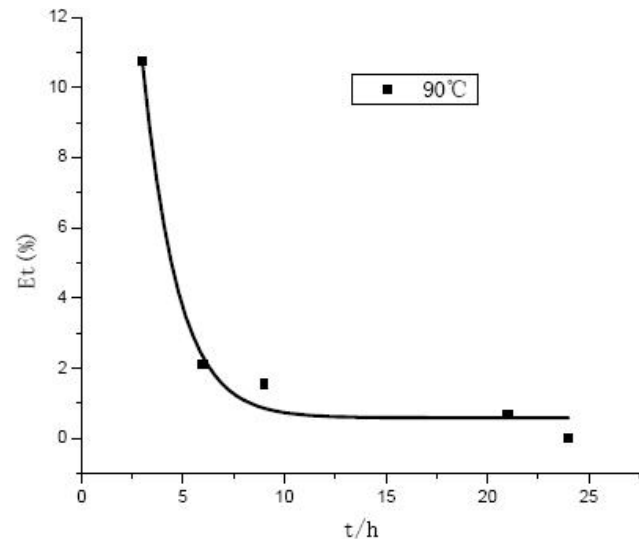**Figure 2 : The curve of residual rate of wood extractives**

Figure 3 : Function of E_t—t at 90°C

And then made a tangent, the slope of the tangent line was $\dfrac{dE_t}{dt}$, its negative value was the reaction rate under that concentration (As shown in Figure 4). Find out $\lg(-\dfrac{dE_t}{dt})$ and $\lg E_t$, then made a figure of $\lg(-\dfrac{dE_t}{dt}) - -\lg E_t$ (As shown in Figure 5). The slope of straight line was the value of reaction order *a*.

The slope value of straight line in Figure 5 was the

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reaction order *a*. By making a tangent of the straight line, the slope value of *a* was 1.02. So reaction rate equation (1) could be turned into:

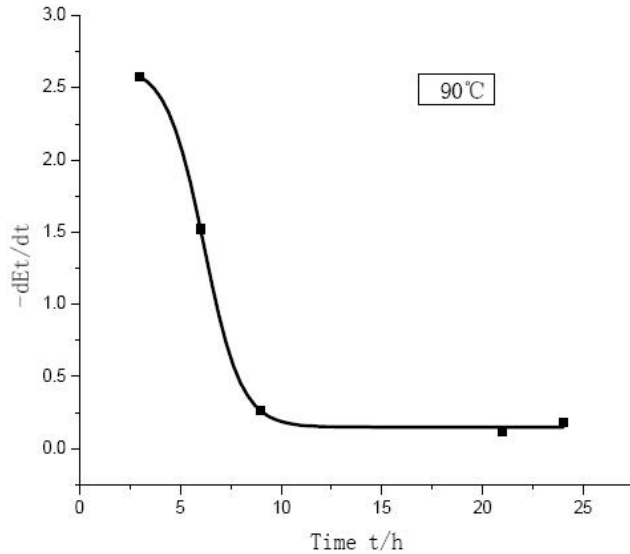$$-\frac{dE_t}{dt} = k_0 \cdot E_t^{1.02} \tag{3}$$

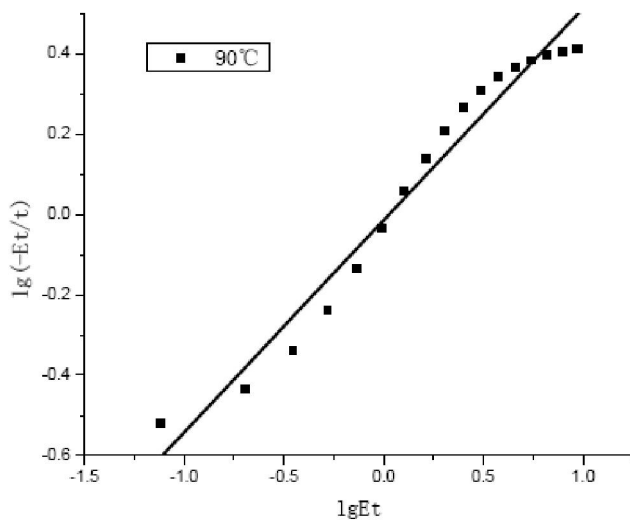**Figure 4 : Function of** $-\dfrac{dE_t}{dt}$ **—t at 90°C**

Figure 5 : Function between $\lg(-\dfrac{dE_t}{dt})$ **and** $\lg E_t$

Determination of the rate constant

From the above, reaction order was confirmed. According to the result, the dissolution reaction of extractives could be dealt with the first order reaction model. Regard rate equation as a first order reaction,

That was: $-\dfrac{dE_t}{dt} = k_0 \cdot E_t$

Integrating the equation above,

$$-\ln\frac{E_t}{E_{t0}} = k_0 \cdot t \tag{4}$$

E_{t0} was the concentration of wood extractives that could leach at the zero moment, E_t was the concentration of wood extractives that could leach out at *t* moment. The concentration of wood extractives was represented by percentage content, that was the content percent of amount of extracts that can leach to absolutely dry wood powder.

Take the experiment at 90°C as an example. The curves of $\ln\dfrac{E_{t0}}{E_t}$ to t at different temperatures were built. The slope of the straight lines was the rate constant k_0 corresponding to temperatures. Based on the fitted data E_t (Figure 2). Diagram of $\ln\dfrac{E_{t0}}{E_t}$ to t was built (Figure 6).
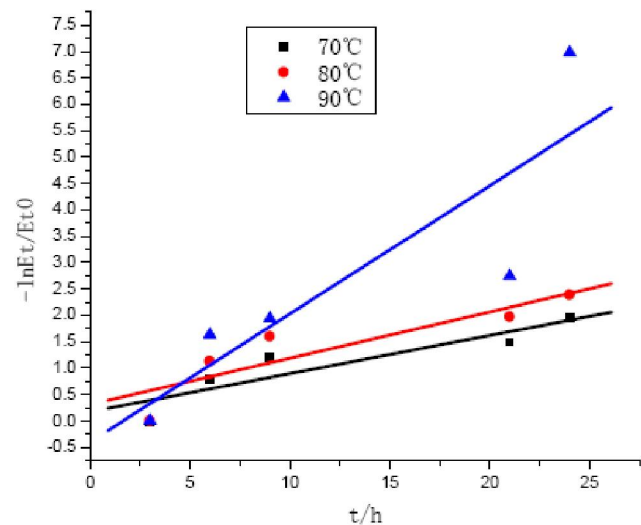
Figure 6 : Function of $\ln\dfrac{E_{t0}}{E_t}$ **to t**

TABLE 3 : The results of the rate constant of wood extractives

Temperature T/K	1/T	k_0/h-1	$\ln k_0$
343.15	0.00291	0.261	-1.343
353.15	0.00283	0.289	-1.241
363.15	0.00275	0.332	-1.103

According to Figure 6, rate constant k_0 under each extraction condition was got, which were listed in

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TABLE 3.

Determination of the activation energy

According to the indefinite integral of Arrhenius equation:

$$\ln k_0 = -\frac{E_a}{RT} + \ln A \qquad (5)$$

E_a was Arrhenius activation energy, which was called activation energy for short, the unit of which was J/mol; A was a pre -exponential factor, which had the same unit as k_0. Depending on the rate constants k_0 corresponding to a series of different temperatures T in Fable 3, the figure of $\ln k_0$—l/T was plotted and shown in Figure 7.
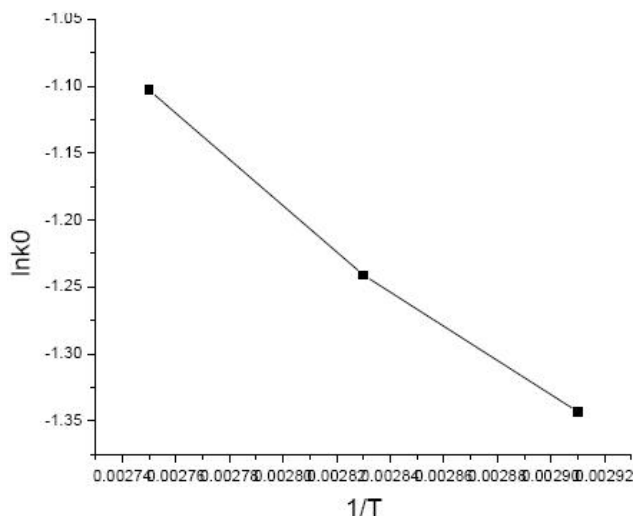

Figure 7 : Relationship between $\ln k_0$ and 1/T

According to Arrhenius equation, the slope of the straight line is the value of activation energy E_a, intercept is *a* pre -exponential factor A.

A regression equation was got from Figure 7

$$\ln k_0 = -\frac{14549.86}{8.314} \cdot \frac{1}{T} + \ln 20.48 (R^2 = 0.993)$$

From the above equation, activation energy of reaction E_a =14549.86J/mol, thepre-exponential factor A =20.48h⁻¹.

CONCLUSION

When *Eucalyptus camaldulensis*biomasswas extracted, the dissolution of wood extractives could be divided into three phases: the rapidly leaching phase, slowly leaching phase and the equilibrium leaching phase.

In the equilibrium leaching phase, wood extractives leaching reached balanced state. When the temperature was high, the wood extractives fast leached. However, wood extractives achieved equilibrium for shorter time, and the residual rate of wood extractives in *Eucalyptus camaldulensis*biomass was less.

The dissolution reaction of extractives could be dealt with the first order reaction model, the overall reaction order was 1.02. The reaction rate increased with increasing temperature, the activation energy (E_a) of reaction was 14549.86J/mol, the pre-exponential factor (A) was 20.48h⁻¹.

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