Study on Optimization of Tung Oil Bleaching and Refining Process Using Response Surface Methodology

Aihua Zhang[1, a], Gaokuan Du[2, b], Zhihong Xiao[1, c], and Changzhu Li[1, d]

[1]Hunan Academy of Forestry, Changsha 410004, China

[2]Chang Sha Universty Sciece&Technology, Changsha 410004, China

[a]zhangaihua909@163.com, [b]1097515922@qq.com, [c]xzhh1015@163.com, [d]lichangzhu2013@aliyun.com

Abstract: Tung oil, as a kind of drying oil, with the influence of water, acid, alkali, or light, is easy to have variation. This research adopts the active carbon decoloring refining process in tung oil refining, and response surface experiment process is adopted to optimize the process. And finally I obtain the best process condition: temperature 80.17 ℃, decoloring time 90.71 min, decoloring dosage 3.49%, and the decolorization rate was 92.48% under the condition. Tung oil were analyzed by gc instrument, and found that the main ingredients is cis, trans, trans - 9,11,13-18 carbon triene acid, with content as high as 70.31%, which determines the physical and chemical properties of tung oil. Through the functional groups absorption peak of tung oil (before and after decolorization) by – IR, founding that the technology can guarantee the quality of tung oil very well.

1. Introduction

The tree is a deciduous tree of euphorbia, and also is known as tung subtree. It is a special product of our country, mainly distributing in China's Yangtze river basin and its south region [1,2]. The particularity of the physical and chemical properties of tung oil has determined the refining process cannot adopt the technology and parameters adopted in common processing such as degumming, alkali refining, deodorization and decolorization. Qiu Yi-zhou [3]had made researches about the infusion of tung oil and decolorization and found that the sulfur element had a significant influence on tung oil curing, and found that the temperature had an important relation with the quality of tung oil. Zhang Min [4] studied the preparation of eleostearic acid and its process, mainly taking temperature, time and PH value into consideration, and found that the reflux time had an important effect on the reaction. Yang Bao-an [5] made a review of the deep processing of tung oil and its comprehensive utilization path, and he thought that improving the quality of tung oil is a driving force in promoting the tung oil industry. Qiu Kai [6] made an explaination on how to improve the quality of tung oil. He argues that excluding the factors such as variety, maturity, removing pigment impurities is also an important step to improve the quality of tung oil. But how to carry out systematic decoloring is not in-depth study.

At present, our country is still in the blank stage for the development of decolorization and refining of tung oil industry system, and only a few scientific research or enterprises that have been scattered in the initial stage [7]. This study started with the low temperature decolorization method, focusing on the quality of the chroma of tung oil processing, and provides some basic theoretical data for the healthy development of tung oil industry in China.

2. Materials and Method

2.1. Materials

AUY-220 electronic analytical balance (Japan Shimadzu); SHZ - D (Ⅲ) circulating water vacuum pump (Gongyi Yu Hua instrument co. LTD.); GCMS-QP2010 gas chromatograph-mass spectrometer (Japan Shimadzu); IS5 Fourier transform infrared spectrometer (American symer fable); Df-101s thermostatic heating magnetic stirrer (zhengzhou Great Wall science and technology co., LTD.).

Crude oil of tung oil (press process, made by Hunan forestry academy)； Activated carbon powder (CP, guoyao chemical reagent co., LTD).

2.2. Method

2.2.1. Method of refined decolorization of tung oil

Accurately weighing and taking a certain amount of tung oil, in the vacuum degree 0.09 MPa, water bath heating to 95 ℃ temperature conditions, removing the residual moisture in oil until the oil level of no longer has bubbles. Cooled to the set temperature, adding a certain amount of adsorbent activated carbon powder under the normal pressure conditions, continuing to vacuumize to 0.09 MPa, and rising to the set temperature, cooling down to 40 ℃ after stirring at a constant speed of a certain duration, breaking the vacuum and filtering, and filtering out adsorbent, finally getting decoloring tung oil after refining.

2.2.2. Temperament analysis method

Chromatographic conditions [8] : FID detector, ov-1 column (30.0m x 0.25mm x 0.25 mu m); Helium as the carrier gas, flow rate of 10.0 mL/min, sample quantity of 1.0 mu, L, injection temperature is 260.0 ℃, the ion chamber temperature 240.0 ℃; Program temperature conditions: temperature, initial temperature of 50.0 ℃ (2.0 min), the heating speed is 10.0 ℃ / min to 190.0 ℃ (10.0 min), a speed is 5.0 ℃ / min to 240.0 ℃ (20.0 min).

Mass spectrometry condition: Scion SQ 4 beam mass spectrometer, electron bombardment (EI) ion source, electron energy 70.0 eV; Quadrupole temperature is 180.0 ℃; Ion source temperature is 250.0 ℃; Quality scan range 33-350 amu.

2.2.3. Fourier infrared FT-IR characterization

The Fourier infrared spectral characterization condition [9]: the detector is the mid-infrared DTGS detector, the wave number scanning range is 400.0cm^{-1}-4000.0 cm^{-1}, and the resolution is 4.0 cm^{-1}.

2.2.4. Calculation method of decolorization rate

The absorbance in the wavelength of 420nm was measured by ultraviolet spectrophotometer. The calculation formula of decolorization rate is as follows:

$$\text{Decolourization Ratio}(\%) = \frac{A - A'}{A} \times 100 \qquad (1)$$

In formula: A is the pre-color absorbance value for tung oil;

A 'absorbance value for tung oil decoloration.

3. Results and analysis

3.1. Experimental results and analysis of the response surface

The three levels of response surface analysis were performed using box-behnken for decolorization temperature (*A*), decolorization time (*B*) and decolorizing agent (*C*). The experimental factors and horizontal codes were shown in table 1.

Table 1 Analytical factors and levels for RSA

level	decolorization temperature(*A*)/℃	decolorization time*(B)*/min	decolorizing agent*(C)*/%
-1	77	85	3.3
0	80	90	3.5
1	83	95	3.7

According to table 1 of tung oil decoloring, there are a total of 17 experimental data points, the results are shown in table 2, the experimental regression model of variance analysis are shown in table 3, the response surface experiment test of significance of regression equation coefficient analysis are shown in table 4.

Table2 Experimental design and results

No.	*A*	*B*	*C*	esterification rate/%
1	80	95	3.7	85.76
2	77	85	3.5	86.35
3	77	90	3.3	86.23
4	80	85	3.7	85.53
5	80	90	3.5	92.34
6	80	90	3.5	92.37
7	77	90	3.7	85.67
8	83	90	3.3	86.69
9	83	95	3.5	87.79
10	80	95	3.3	88.45
11	80	85	3.3	84.34
12	80	90	3.5	92.27
13	80	90	3.5	92.31
14	83	85	3.5	87.47
15	80	90	3.5	92.17
16	77	95	3.5	87.46
17	83	90	3.7	86.27

Table 3 ANOVA for the regression model

soruce of variation	quadratic sum	degree of freedom	mean square	F value	P value
model	139.51	9	15.50	80.52	＜0.0001
A	0.79	1	0.79	4.09	0.0828
B	4.16	1	4.16	21.62	0.0023
C	0.77	1	0.77	3.99	0.0858
AB	0.16	1	0.16	0.81	0.3979
AC	4.90E-003	1	4.90E-003	0.025	0.8778
BC	3.76	1	3.76	19.55	0.0031
A^2	26.52	1	26.52	137.76	＜0.0001
B^2	30.80	1	30.80	160.00	＜0.0001
C^2	59.44	1	59.44	308.75	＜0.0001
residual	1.35	7	0.19		

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Lack of fit	1.11	3	0.37	6.27	0.0542
Pure Error	0.24	4	0.059		
total dispersion	140.86	16			
R-Squared=0.9904; *Adj R-Squared*=0.9781; *Pred R-Squared*=0.8711; *Adeq Precision*=23.307 *Std. Dev*=0.44; *Mean*=88.26; C.V.%=0.50					

Table4 Test of significance for regression equation coefficients

divisor	Coefficient estimate	degree of freedom	standard error	95% confidence interval low value	95% confidence interval high value
intercept	92.46	1	0.20	92.02	92.95
A	0.31	1	0.16	-0.053	0.68
B	0.72	1	0.16	0.35	1.09
C	-0.31	1	0.16	-0.68	0.057
AB	-0.20	1	0.22	-0.72	0.32
AC	0.035	1	0.22	-0.48	0.55
BC	-0.97	1	0.22	-1.49	-0.45
A^2	-2.51	1	0.21	-3.02	-2.00
B^2	-2.70	1	0.21	-3.21	-2.20
C^2	-3.76	1	0.21	-4.26	-3.25

In this paper, the data of 17 experimental points for the decoloration of tung oil in table 2 were obtained by quadratic multiple regression fitting, and the regression model was obtained as follows：

$$\mathrm{Y} = 92.46 + 0.31 \times A + 0.72 \times B - 0.31 \times C - 0.20 \times A \times B + 0.035 \times A \times C$$
$$-0.97 \times B \times C - 2.51 \times A^2 - 2.70 \times B^2 - 3.76 \times C^2 \quad (2)$$

In this experiment, the regression model of P < 0.0001, R2= 0.9904, indicating that the regression model fits well, by which tung oil decolorization process can be analyzed and predicted.

By Fig. 1, Fig. 2 and Fig. 3 showing that tung oil bleaching refining process of decoloring rate (Y) and decoloring temperature (A), bleaching time and decoloring agent (B) (C) prior to the balance point is proportional to the relationship. The best decoloring process parameters: decoloring temperature 80.17 ℃, decoloring time 90.71 min, decoloring agent usage 3.49%. Three parallel verification experiments were conducted under the optimized decolorization conditions, and the results showed that the decolorization rate of tung oil was 92.48%, which was close to the predicted value of 92.55%, indicating that the regression equation fit well.

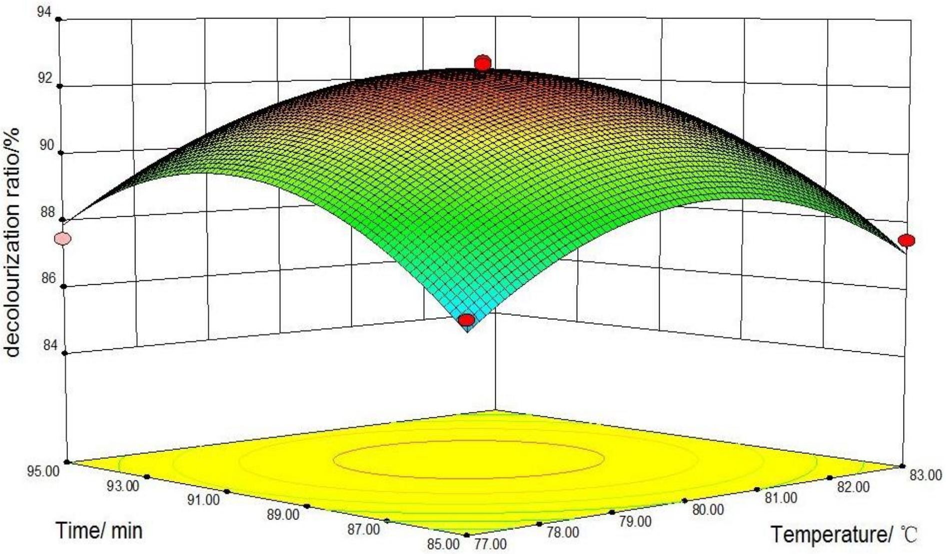

Fig.1 Response surface map: A Temperature & B Time

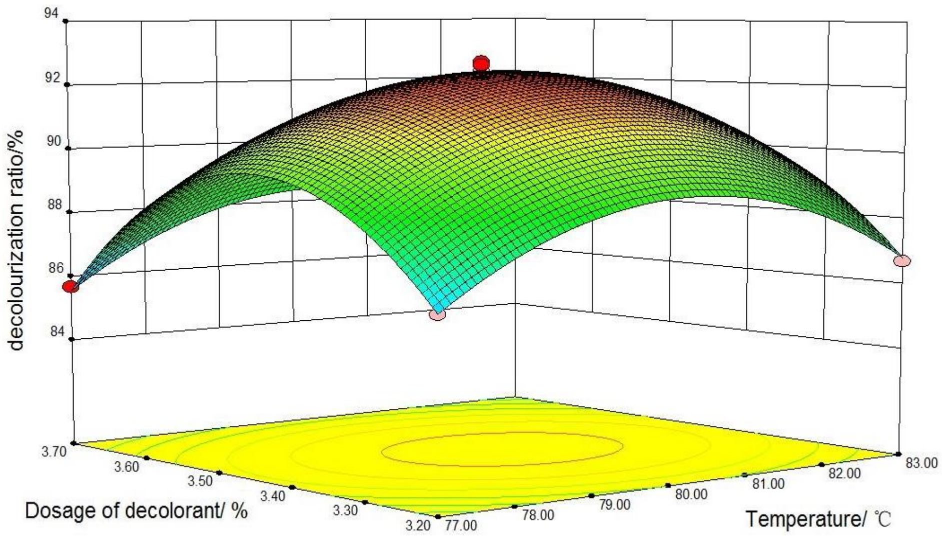

Fig.2 Response surface map: A Temperature & C decolorizer dosage

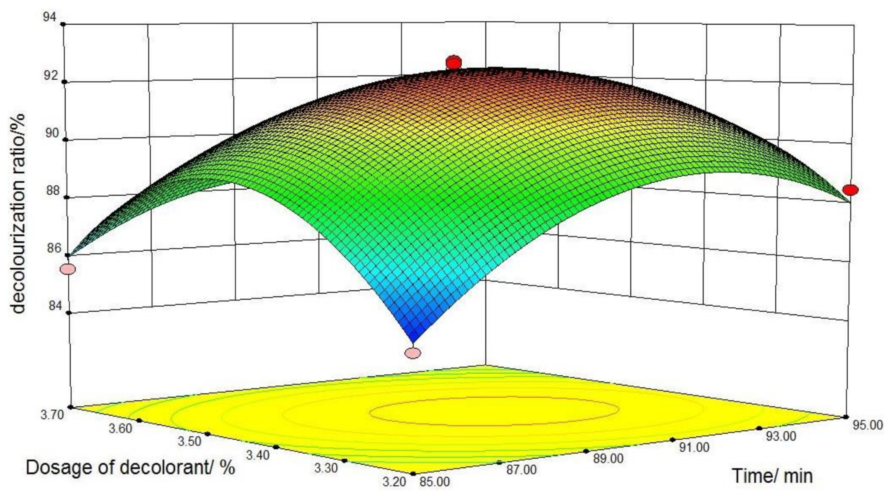

Fig.3 Response surface map: B Time & C decolorizer dosage

3.2. Analysis of tung oil temperament spectrogram

The Fig. 4 shows that tung oil fatty acid composition is mainly contains alpha eleostearic acid, beta eleostearic acid, linoleic acid, oleic acid, palmitic acid, stearic acid, etc., the alpha eleostearic acid (70.31%), beta eleostearic acid 4.62%, linoleic acid 8.92%, oleic acid 6.72%, 2.83% palmitic acid, stearic acid 3.74%. Tung oil acid is a kind of 18-carbon conjugated trienoic acid. The high content of tung oil determines the difference between the basic physical and chemical properties of tung oil and the conventional oil.

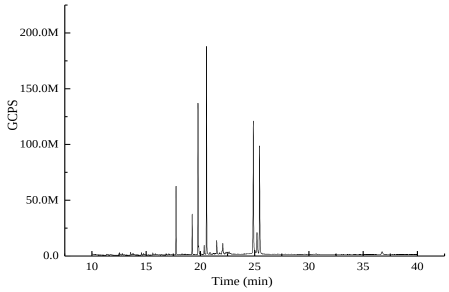

Fig.4 GC-MS of Tung oil

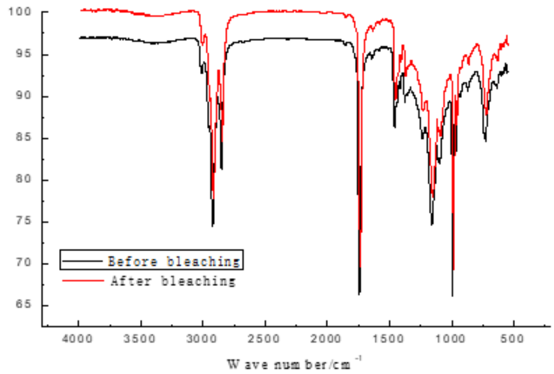

Fig.5 FT-IR of Tung oil

3.3. Tung oil infrared spectrum

It can be seen from Fig. 5 that the infrared spectrum before and after the decolorization of tung oil is almost unchanged, indicating that the refining process has little effect on the tung oil molecules. The main component for Tung oil fatty acid is alpha eleostearic acid, a kind of cis, trans, trans - 9,11,13- 18 carbon triene acid, there are three conjugated double bonds in tung oil acid molecules.With infrared spectrum Fig. 5 shows: trans double bond C - H stretching vibration characteristic absorption peak at 3010 cm^{-1}; The absorption peak of flexural vibration in c-h is located at 1370 cm^{-1}. The absorption peak of C=C double bond is located at 1695 cm^{-1} ~ 1630cm^{-1}. The absorption peak of c-o in triglyceride is at 1300 cm^{-1}~1000 cm^{-1}.

4. Conclusions

In this study, the refining and discoloration of tung oil by activated carbon were used, and the process conditions were optimized, and the conclusions were drawn as follows:

(1) response surface experiment is adopted to Tung oil refining bleaching and obtain optimized process conditions as follows: the temperature of 80.17 ℃, decoloring time 90.71 min, decoloring agent usage 3.49%, under the condition of which, the decolorization rate is 92.48%;

(2) By comparing the differences of the absorption peaks of the oil molecules in the oil molecules before and after decolorization, the effect of adsorption decolorization on the essence of tung oil was found to be negligible.

Acknowledgements

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