Artigos

Use of experimental design techniques for the optimization of the resin distillation process of *Pinus elliottii*

Utilização de técnicas de planejamento experimental para a otimização do processo de destilação de resina de *Pinus elliottii*

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ABSTRACT

In the last decades, the resin product sector in Brazil is demonstrating a growing demand perspective for resin gum producers, what requires advances in the technical part of the extraction and purification processes. This work aimed to analyze, through experimental design techniques, the washing and distillation processes of the *Pinus elliottii* oleoresin. The natural resin was collected in the coastal region of Rio Grande do Sul state, Brazil. The results of the washing step revealed that the linear with second-order interactions was the empirical model that best suited for this study. Therefore, the optimal test was determined with the following factors: temperature of 50ºC, time of 20 min, and 20% turpentine used for dilution. For the distillation process, the best model was the linear without interactions taking into account the Monetary Value (Real – R$) response per 100 g of processed resin. Thus, it was determined that the optimum region obtained the following factors: temperature between 156 and 170 ºC and time between 61 and 100 min. Therefore, the use of experimental design techniques enabled to propose some alternatives on the processing of natural resin to the producer, what consequently caused the increase in its added value to the marketed product.

Keywords: Resination; Pitch; Turpentine

RESUMO

Nas últimas décadas, o setor de produtos de resina no Brasil está demonstrando uma perspectiva de demanda crescente para os produtores de goma de resina, o que exige avanços na parte técnica dos processos de extração e purificação. Este trabalho teve como objetivo analisar, através de técnicas de planejamento experimental, os processos de lavagem e destilação da oleorresina de *Pinus elliottii*. A resina natural foi coletada na região costeira do estado do Rio Grande do Sul, Brasil. Os resultados da etapa de lavagem revelaram que as interações lineares de segunda ordem foi o modelo empírico mais adequado para este estudo. Portanto, o teste ideal foi determinado com os seguintes fatores: temperatura de 50ºC, tempo de 20 min e 20% de terebentina utilizada para a diluição. Para o processo de destilação, o melhor modelo foi o linear sem interações, considerando a resposta do Valor Monetário (Real – R$) por 100 g de resina processada. Assim, determinou-se que a região ótima obteve os seguintes fatores: temperatura entre 156 e 170ºC e tempo entre 61 e 100 minutos. Portanto, o uso de técnicas de planejamento experimental permitiu propor ao produtor algumas alternativas no processamento de resina natural, o que consequentemente causou o aumento do valor agregado ao produto comercializado.

Palavras-chave: Resinagem; Breu; Terebentina

1 INTRODUCTION

Brazil has the second-largest forest area in the world, covering almost 60% of the national territory. The data obtained by the Food and Agriculture Organization (FAO) reveal that the practice of silviculture in the Brazilian territory is growing and totals 494 million hectares of forests (FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS, 2015). In 2011, the Ministry of Agriculture, Livestock, and Supply (MAPA) announced that the forestry sector is strategic for Brazil since it has indicated environmental and mainly economic benefits due to alternative logging (BRASIL, 2011). In this context, the resin was one of the important activities for the success of the forestry sector. This activity increased in the 1970s through tax incentive laws for the planting of *Pinuselliottii*. However, there was a slight improvement in the exploration stages (HASELEIN *et al*., 2000; MISSIO *et al*., 2015).

Currently, Brazil is the world's second-largest producer of resin, coming after China. According to the Association of Resinators of Brazil (ARESB), the Brazilian production of resin gum for the 2017/18 crop is estimated at 185,692 tons, double the

amount obtained in the 2014/15 crop (ASSOCIAÇÃO DOS RESINADORES DO BRASIL, 2018; CASSOL *et al*., 2019). Natural resin is a yellowish-white flammable substance, of noticeable fluidity, insoluble in water, and has several industrial applications. In the initial process of the resin, different extraction methods are used, such as the French system and the American system. The latter system consists of using an acidic paste in the "streaking" process containing 30 to 60% sulfuric acid (H_2SO_4) (SUKARNO *et al*., 2015).

The economic potential of the resin is due to its main components, pitch, and turpentine. The average yield of the separation process is 79-88% for pitch and 7-15% for turpentine, in which the highest-selling value corresponds to the lowest yield being sold at R\$ 95 L^{-1} (US\$ 18.23 L^{-1}). Pitch is marketed according to criteria that evaluate its quality. To qualify it, the number of saponification, acidity, color, and the softening point is analyzed. This material is a solid, glassy, brittle substance with color that varies from amber to yellow. Pitch is used in the manufacture of glues for paper, varnishes, paints, rubbers, adhesives, and cosmetics. Turpentine, on the other hand, is characterized by its volatility and intense odor and it can be used in the manufacture of solvents, paints, varnishes, disinfectants, soaps, fragrances, and synthetic camphor (BRITO; BARRICHELO; GUTIERREZ, 1980; KOLICHESKI, 2006).

Given the above, there are countless possibilities of using the constituents of the resin in industrial applications, being essential the evaluation of means that can increase production and purity and adding value to the products of the sector (MARCELINO; FENNER, 2005; GEORGIN, 2014; AMPESSAN *et al*., 2015). However, it is still necessary to promote studies aimed at improving the resin steps, starting with the extraction process. This process many times has no pattern of the collection in the exploration areas what results in commercializing the natural resin with dirt and impurities. Consequently, it decreases the sale values to the industries and even may cause the return of the product. Therefore, it is extremely important to improve the processes of extraction and partial purification of the resin. As a result, there will be

progress in the activity, increasing production, and possibly adding commercial value to it. Thus, the objective of this study was to analyze, through experimental design techniques, the washing and distillation processes of the *Pinuselliottii* oleoresin.

2 MATERIAL AND METHODS

This study used natural resin collected in the coastal plain region of Rio Grande do Sul state (Latitude 31˚17'14" South and Longitude 51˚05'37" West), obtained from *Pinuselliottii* tree incisions, with the application of 30% H_2SO_4 acid paste. The pine trees were aged between 18-20 years, with diameters between 15-30 cm, and the soil type of the planted area was sandy (FUSATTO *et al*., 2013; SCHNEIDER *et al*., 2013). Figure 1 illustrates the raw resin collection container and the process of applying the acid paste to the panel. All experimental steps were performed at the Laboratory of Simulation and Process Development (LSDP) of the Federal University of Rio Grande (FURG), in the Campus of Santo Antônio da Patrulha, Rio Grande do Sul state, Brazil.

Figure 1 – Incision process (a) and application of acid paste on the panel (b)
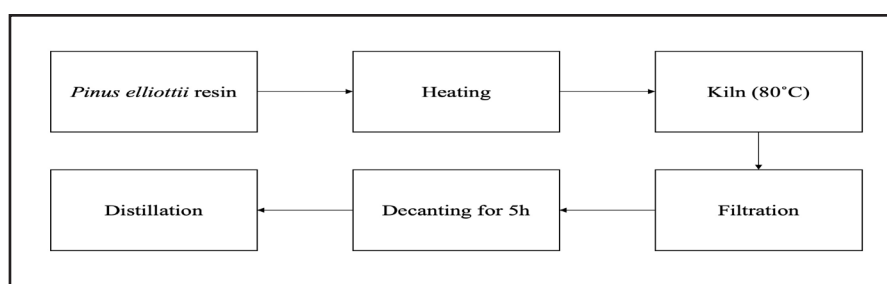

Source: Authors (2019)

2.1 Experimental procedure of distillation of natural resin

The distillation equipment consisted of a heating blanket connected to a flask with three outlets containing a total volume of 500 mL. The distillation column was coupled to one of the outlets. In the other outlet of the balloon, a thermometer was added to measure the boiling temperature. In the third outlet, a lid was placed to add and remove the material without needing to disassemble the column. The crude resin from the study site was poured into a reservoir container for heating. In this step, oxalic acid was added to precipitate the iron contained in the resin and diatomaceous earth that acted as a filter aid (ASSUMPÇÃO, 1978; BRITO; BARRICHELO; GUTIERREZ, 1980).

Turpentine was added to the resin dilution, approximately 30% of the total, in order to reach the desired temperature of 80°C. The vessel remained for 15 minutes at 80°C. Then, the heated solution was filtered hot. After the filtration step, the filtrate substance was collected in a vessel that remained to settle for five hours at 80°C (ASSUMPÇÃO, 1978). After the decantation period, the resin was placed in a 500 mL flask, and it was subjected to vacuum distillation (Figure 2). The heating of the blanket was achieved with temperatures between 130 and 170°C. The distillation was interrupted according to the time of each trial. After distillation, the water was separated from turpentine by decantation (BRITO; BARRICHELO; GUTIERREZ, 1980).

Figure 2 – Schematic representation of the distillation process of *in natura* resin

Source: Authors (2019)

Experimental design was used, following the laboratory procedure, in the two stages under study. These steps consisted of washing, with conditions varying temperature, time, and percentage of turpentine, and distillation, with conditions varying the time and temperature at the base of the column. Experimental design is a tool used in processes involving analysis and optimization of operations. It allows to evaluate the effects among a set of variables involved in the process, taking advantage of a small number of experimental tests (BOX; HUNTER; HUNTER, 2005; MONTGOMERY, 2012; FERNANDES *et al.*, 2016; LOPES *et al.*, 2016; SILVA JÚNIOR *et al.*, 2018).

2.2 Experimental design of the washing step

The influence of the following process variables was evaluated: A) temperature, B) time, and C) turpentine percentage. The analyzed factors and the corresponding coded statistical indices are presented in Table 1. Table 2 demonstrates the complete factorial design matrix 2^3, which was used in the experimental trials.

Table 1 – Coded factors and levels used for the wash step

Factors	CodedLevels (-1)	CodedLevels (0)	CodedLevels (+1)
Temperature (°C)	50	70	90
Time (min)	10	15	20
Turpentine (%)	20	25	30

Source: Authors (2019)

Table 2 – Matrix of complete factorial design 2^3 with triplicate at central point

Assay	Temperature (°C)	Time (min)	Turpentine (%)
1	-1	-1	-1
2	+1	-1	-1
3	-1	+1	-1
4	+1	+1	-1
5	-1	-1	+1
6	+1	-1	+1
7	-1	+1	+1
8	+1	+1	+1
9	0	0	0
10	0	0	0
11	0	0	0

Source: Authors (2019)

2.3 Experimental design of the distillation step

The influence of the following process variables was evaluated: A) temperature at the base of the column and B) time. The analyzed factors and the corresponding coded statistical indices are presented in Table 3. In addition, Table 4 illustrates the complete factorial design matrix 2^2, which was used in the experimental trials.

Table 3 – Coded factors and levels used for the distillation step

Factors	CodedLevels (-1)	CodedLevels (0)	CodedLevels (+1)
Distillation column base temperature (ºC)	130	150	170
Time (min)	40	70	100

Source: Authors (2019)

Table 4 – Matrix of complete factorial design 2^2 with triplicate at central point

Assay	Distillation column base temperature (ºC)	Time (min)
1	-1	-1
2	+1	-1
3	-1	+1
4	+1	+1
5	0	0
6	0	0
7	0	0

Source: Authors (2019)

A 2^n complete factorial design (triplicate at the central point) was adopted together with the use of Response Surface Methodology (RSM), in order to obtain the optimal operating conditions. The results were analyzed by using the Statistica 8.0® software (BOX; HUNTER; HUNTER, 2005).

3 RESULTS AND DISCUSSION

3.1 Experimental design of the natural resin washing process

At this stage of the *Pinus elliottii* resin washing process, the response variable was the amount of resin after the filtration procedure. The experimental design techniques were

used to obtain an optimal region of the process. Table 5 presents a matrix of complete factorial experimental design 2^3, with triplicate at the central point.

Table 5 – Matrix of complete factorial experimental design 2^3 with triplicate at the center point and the response

Assay	Temperature (ºC)	Time (min)	Turpentine (%)	Resin amount after filtration (g)
1	-1 (50)	-1 (10)	-1 (20)	96.922
2	+1 (90)	-1 (10)	-1 (20)	92.856
3	-1 (50)	+1 (20)	-1 (20)	97.726
4	+1 (90)	+1 (20)	-1 (20)	90.281
5	-1 (50)	-1 (10)	+1 30)	93.781
6	+1 (90)	-1 (10)	+1 (30)	94.563
7	-1 (50)	+1 (20)	+1 (30)	94.502
8	+1 (90)	+1 (20)	+1 (30)	91.587
9	0 (70)	0 (15)	0 (25)	93.661
10	0 (70)	0 (15)	0 (25)	94.402
11	0 (70)	0 (15)	0 (25)	93.405

Source: Authors (2019)

Through the results obtained in Table 5, a statistical analysis of the effects of the three independent variables studied was performed, obtaining the response variable. The model chosen to be used was based on the statistical indices obtained through the analysis of variance (ANOVA) and the coefficient of determination (R^2). The chosen model was linear with second-order interactions. Next, in Table 6, we observe the values of $F_{Calculated}$ e $F_{Tabulated}$ corresponding to the models, in addition to their coefficient of determination.

Table 6 – Comparison between empirical models regarding resin quantity response

Model	R^2	Regression/Residues		Lack of fit/Pure error	
Linear with out interactions	0.598	F_{Calc}	3.476	F_{Calc}	12.969
		F_{Tab}	4.347	F_{Tab}	19.296
Linear with second-order interactions	0.908	F_{Calc}	23.061	F_{Calc}	2.659
		F_{Tab}	4.347	F_{Tab}	19.296
Linear with third-order interactions	0.985	F_{Calc}	30.045	F_{Calc}	0.340
		F_{Tab}	8.887	F_{Tab}	18.513

Source: Authors (2019)

Where: Distribution value $F_{Tabulated}$ obtained from MONTGOMERY (2012).

In Table 6, it is possible to compare the determination coefficients and the values of $F_{Calculated}$ and $F_{Tabulated}$ between empirical models. It may also be assumed that a relatively high R^2 has determined the choice of the second-order model. The table also presents the ratio of the distribution values of $F_{Calculated}$ Regression/Residues 5.0 times higher than the distribution value $F_{Tabulated}$ at a confidence level of 95% of the process. One of the justifications of these results is to better present the relationship between the $F_{Calculated}$ for Adjustment/Pure Error, which is less than the distribution value of $F_{Tabulated}$. Thus, it is assumed that the model represents well the relationship between effects and response. The non-use of the third-order and the linear model without interactions is due to the low R^2 (59.8%) and the problems linked in the experiment, respectively. Thus, it was calculated the effects and statistical indices for the selected model, which is observed in Table 7. Furthermore, the Pareto graph was performed to verify the significance of the factors (Figure 3).

Table 7 – Effect calculations and statistical indices

Factors	Effect	Standard deviation	Value of p	Confidence limits -95%	+95%
Average/interactions	93.971	0.156	0.000003	93.299	94.643
(A) Temperature (°C)	-3.411	0.366	0.011326	-4.986	-1.835
(B) Time (min)	-1.006	0366	0.110769	-2.581	0.568
(C) % Turpentine	-0.838	0.366	0.149293	-2.413	0.737
Interaction between (A) and (B)	-1.769	0.366	0.040267	-3.344	-0.193
Interaction between (A) and (C)	2.344	0.366	0.023530	0.769	3.919
Interaction between (B) and (C)	-0.121	0.366	0.772444	-1.696	1.454

Source: Authors (2019)

Figure 3 – Pareto graph regarding resin quantity response after filtration
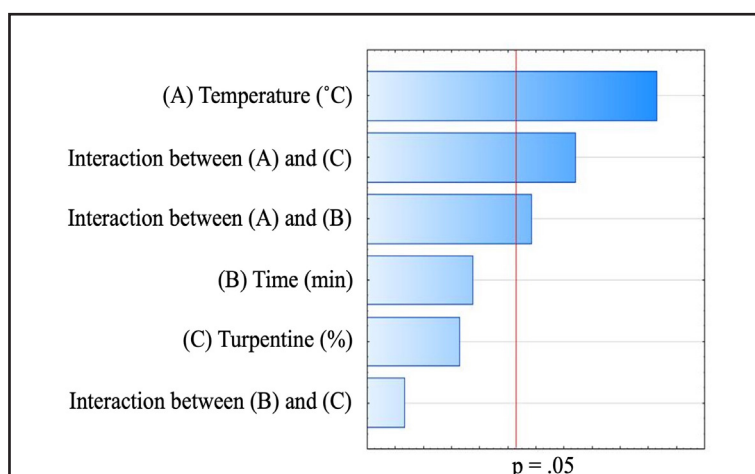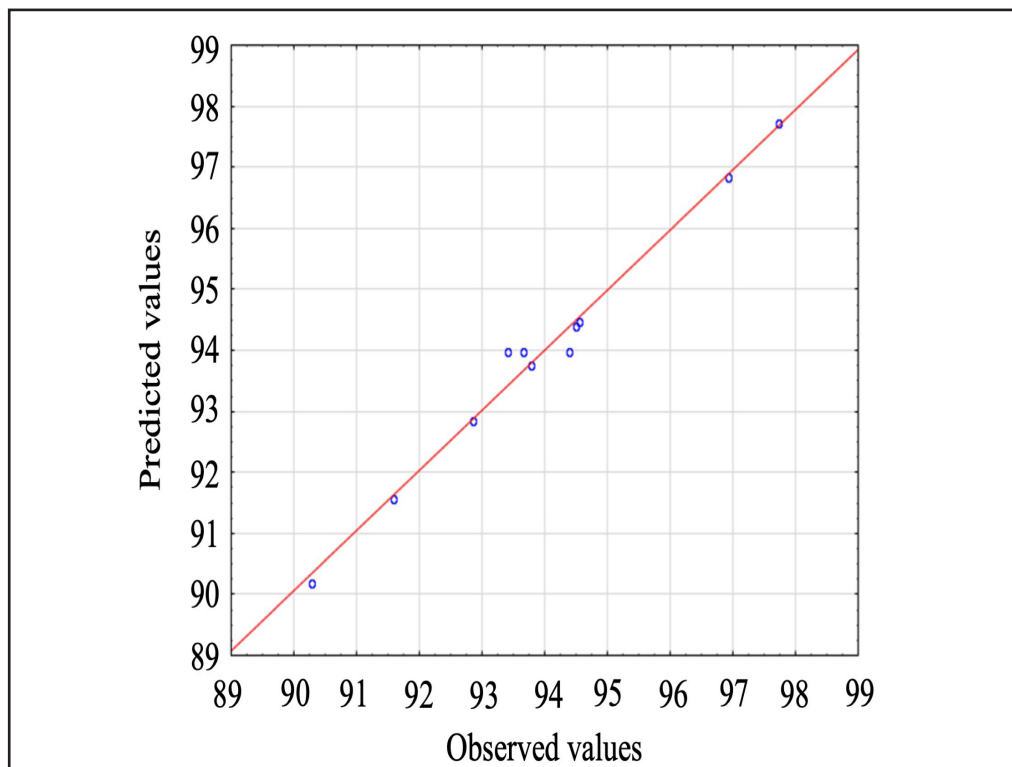

Source: Authors (2019)

Analyzing Table 7 and Figure 3, it appears that the terms (A), the interaction between (A) and (C), and the interaction between (A) and (B) are significant, as seen by the statistical indices presented. Furthermore, the low residue is verified in Figure 4, the graph of values observed by predicts. Thus, it was obtained the coded empirical model for the response variable under study. It was also used only significant factors, as shown in Table 6 and Figure 3 what is demonstrated in Equation 1. Thus, variables A, B, and C were used to generate the response cube (Figure 5) in relation to the amount of resin.

$$Y = 93.97 - 1.70A - 0.88AB + 1.17AC \tag{1}$$

Where: Y is the amount of resin (g), A is the temperature (°C), B is the time (min), and C is the % turpentine added in the process.

Figure 4 – Graph of predicted values by the observed ones for resin quantity response after filtration

Source: Authors (2019)

Analyzing the RC, it appears that the sample that has the largest amount of resin is at point -1 (% turpentine), +1 (time in minutes), and -1 (temperature in °C). It corresponds to test 3, in which lower temperature, longer time, and lower percentage of turpentine were used for dilution. Thus, Table 8 indicates the analysis of variance (ANOVA) used to describe the empirical model in relation to the resin quantity response after filtration.

Figure 5 – Response Cube (RC) for coded factors temperature, time, and % turpentine relative to response
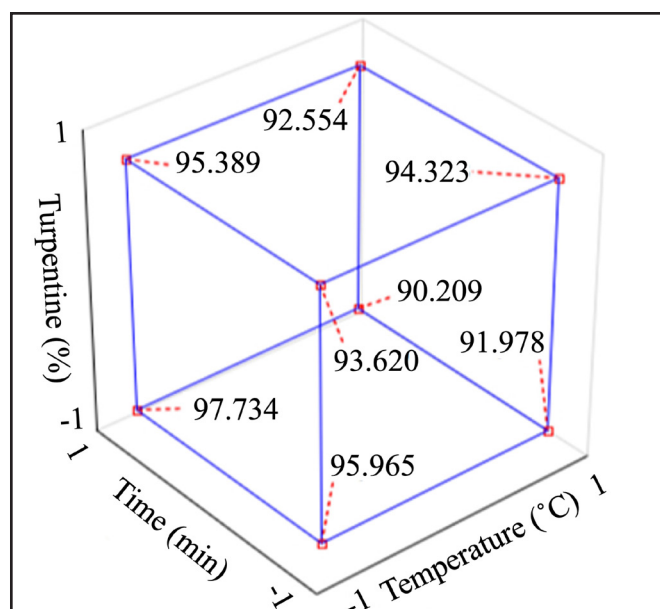
Source: Authors (2019)

Table 8 – Analysis of variance for the amount of resin

Variation Source	Quadratic Sum	Degree of Freedom	Quadratic Averages	$F_{Calculated}$	$F_{Tabulated}$
Regression	40.521	3	13.507		
Residues	4.100	7	0.585	23.061	4.347
Lackof Fit	3.563	5	0.712		
PureError	0.536	2	0.268	2.658	19.296
Total	48.720				

Source: Authors (2019)

Where: Variation explained: 91.58%; Maximum variation explained: 98.89%

Table 8 reveals that the Pure Error found has a low value and the variation explained by the model is high compared to the maximum explainable variation, which is close to 100%. Also, it appears that the residues, as seen in Figure 3, are low.

3.2 Experimental design of *Pinus elliotti* resin distillation process

At this stage, the *Pinus elliottii* distillation process was performed with the aid of experimental design techniques. A complete factorial experimental design matrix 2^2, with triplicate at the central point, was used for the tests (Table 9), which included an optimal region of the process. The response variable was Monetary Units (R$) per 100 g of processed resin.

Table 9 – Matrix of complete factorial design 2^2 with triplicate at central point

Assay	Distillation column base temperature (ºC)	Time (min)	Pitch Quantity (g)	Turpentine Quantity (g)	R$ 100 g of resin
1	-1 (130)	-1 (40)	68.304	10.220	2.179
2	+1 (170)	-1 (40)	65.503	15.144	2.587
3	-1 (130)	+1 (100)	68.636	13.092	2.453
4	+1 (170)	+1 (100)	65.330	18.341	2.881
5	0 (150)	0 (70)	66.501	15.553	2.643
6	0 (150)	0 (70)	68.211	13.765	2.507
7	0 (150)	0 (70)	66.364	14.908	2.580

Source: Authors (2019)

Where: Pitch commercial value (Octubre 3, 2018): R$ 0.018 g^{-1}; Turpentine commercial value (Octubre 3, 2018): R$ 0.093 g^{-1}.

Through the results obtained in Table 9, it was performed the statistical analysis of the effects of the two independent variables studied what obtained the response variable. The model chosen to be used was based on the statistical indices obtained through the analysis of variance and the coefficient of determination (R^2). The chosen model was the linear one without interactions. In Table 10, presented the values of $F_{Calculated}$ and $F_{Tabulated}$ corresponded to the models, in addition to their coefficient of determination.

From Table 10, it is possible to compare the determination coefficients and the values of $F_{Calculated}$ and $F_{Tabulated}$ between empirical models. The linear model without interactions was chosen due to the determination of a relatively high R^2. It also has the relation of the distribution values of $F_{Calculated}$ for Regression/Residues 5.0 times higher than the distribution value $F_{Tabulated}$ at a confidence level of 95% of the process. One of the justifications to these results is to better present the relationship between the $F_{Calculated}$ for Adjustment/Pure Error, which is 37.0 times lower than the distribution value of $F_{Tabulated}$. Thus, it is assumed that the model represents well the relationship between effects and response. it was calculated the effects and statistical indices for the selected model, as observed in Table 11. The Pareto graph was performed (Figure 6) to verify the significance of the factors.

Table 10 – Comparison between empirical models regarding the response of R$ per 100 g of processed resin

Model	R^2	Regression/Residues		Lack of Fit/Pure Error	
Linear with out interactions	0.94861	F_{Calc}	36.637	F_{Calc}	0.504
		F_{Tab}	6.944	F_{Tab}	19.000
Linear with second-order interactions	0.94862	F_{Calc}	18.458	F_{Calc}	0.987
		F_{Tab}	9.277	F_{Tab}	18.513

Source: Authors (2019)

Where: Distribution value $F_{Tabulated}$ obtained from Montgomery (2012).

Table 11 – Calculation of effects and statistical indexes

| Factors	Effect	Standard Deviation	Value of p	Confidence Limits -95%	+95%
Average/interactions	2.547	0.025	0.000102	2.436	2.657
(A) Distillation column base temperature	0.418	0.068	0.025502	0.125	0.710
(B) Time	0.284	0.068	0.052916	-0.008	0.576

Source: Authors (2019)

Observing Table 9 and Figure 6, it is assumable that the terms (A) and (B) are significant even though variable (B) was slightly higher than 0.05, as seen by the statistical indices presented. In addition, in Figure 7, the graph of values observed by predicts shows the low residues. Thus, it was obtained the coded empirical model for the response variable under study. It was used significant factors, as shown in Table 9 and Figure 6, which may be observed in Equation 2. Thus, variables A and B were used to generate the level curve (Figure 8) in relation to the monetary unit (R$) per 100 g of processed resin.
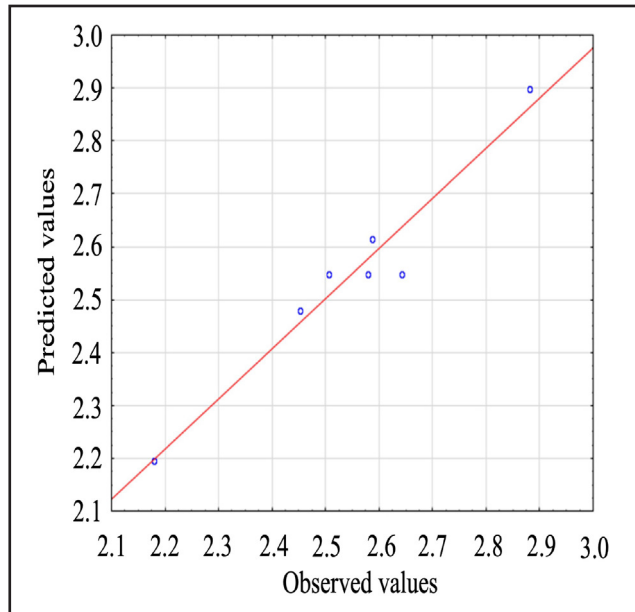
$$Y = 2.547 + 0.209A + 0.142B \tag{2}$$

Where: Y is R$ per 100 g of processed resin, A is the column base temperature (°C), and B is time (min).

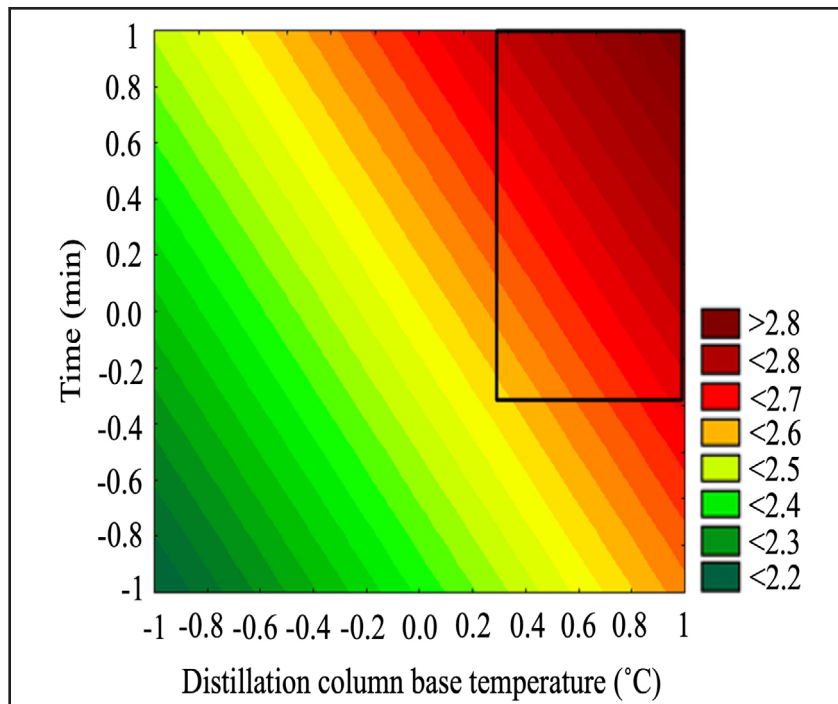Figure 6 – Pareto chart regarding the response of R$ 100 g^{-1} of processed resin
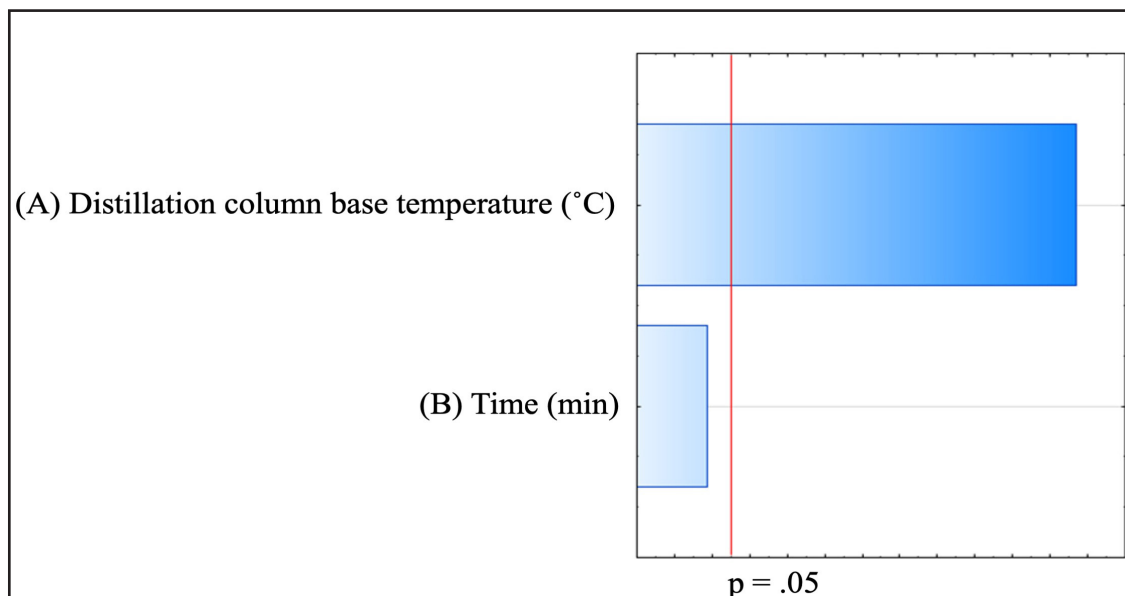
Source: Authors (2019)

Figure 7 – Graph of predicted values by observed in relation to the response of R$ per 100 g of processed resin

Source: Authors (2019)

Figure 8 – Level curves for the coded factors distillation column base temperature and time in relation to the response

Source: Authors (2019)

It can be observed, by analyzing the level curves for the chosen empirical model in Figure 8, that the experiment that has the highest Monetary Value (R$) per 100 g of processed resin has the coded levels +1.0 for distillation column base temperature and +1.0 for time, assay 4. It is due to be the best yield for the turpentine component, which has the highest marketable value. However, there is an optimal region for high response values, which is between -0.3 and 1.0 for time and between 0.3 and 1.0 for the distillation column base temperature. Thus, Table 12 demonstrates the analysis of variance used to describe the empirical model in relation to the response (R$) per 100 g of processed resin.

Table 12 – Analysis of variance for the value in R$ per 100 g of processed resin

Variation Source	Quadratic Sum	Degree of Freedom	Quadratic Averages	$F_{Calculated}$	$F_{Tabulated}$
Regression	0.255	2	0.127		
Residues	0.013	4	0.003	36.637	6.944
Lackof Fit	0.004	2	0.002		
PureError	0.009	2	0.004	0.504	19.000
Total	0.283				

Source: Authors (2019)

Where: Variation explained: 95.07%; Maximum variation explained: 96.73%.

In Table 12, it can be noted that the quadratic sum of the errors is small, which indicates that the model is relevant. In addition, it is found that the Pure Error encountered has a low value. It is assumable that the regression is significant and can be used for prediction purposes. The variation value explained by the model is high compared to the maximum explainable variation, which is approximately 97%. Furthermore, it appears that the residues, as seen in Figure 6, are low. Fusatto *et al*. (2013) tested different stimulating pastes for resin, in which the yield for the pitch was 75.49% and for turpentine, 10.37%. In comparison to the present study, assay 4 showed 65.33% for pitch and 18.34% for turpentine, with a response of R$ 2.88 (US$ 0.55) per 100 g of processed resin.

4 CONCLUSIONS

Results demonstrated that for the present study, the experimental design of the washing step, an initial pre-distillation procedure, test 3 (temperature 50 °C, time 20 min, and 20% turpentine used for dilution) obtained higher amount of resin gum after the filtration procedure for the *Pinuselliottii.* For distillation the Monetary Value (R$) per 100 g of processed resin gum was verified, which has an optimal region of temperatures between 156 and 170ºC and time between 61 and 100 min. The region obtained the highest revenue from the yield of pitch and turpentine due to reaching the highest percentages of turpentine in the trials since it has the highest commercialization value. Therefore, it became possible, with the use of experimental design techniques, to provide the producer alternatives to a natural resin processing and an increased value added to the marketed product.

ACKNOWLEDGMENT

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