Use of thermogravimetry analysis to quantify total volatile fraction in pine resin

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Abstract

Pinus species exhibit fast growth and are good producers of wood, cellulose and resin. Brazil is the second largest producer of resin. The People's Republic of China is the main producer with approximately 90% world's resin production. Turpentine, volatile fraction, and rosin, solid fraction, are two major fractions or resin. The distillation process continues up to 170° C can be extracted about 95% of the total gum turpentine resin, preserving its constituents. There is little research using thermal analysis to study pine resin properties. This work involved evaporating volatile fraction of resins in an oven at 170 ºC consisted of 20 different samples from *Pinus caribaea* var. *hondurensis* and was compared with results obtained in thermal analysis to quantify the same fraction for each one. The volatile fraction in the oven (170 ºC) was from 14.69% to 24.05%. This fraction obtained through thermogravimetric analysis (TGA) was from 13.37% to 23.64%. The results demonstrate that the TGA technique is capable of accurately determining the volatile and non-volatile fractions of the resin and this technical proved to be suitable for further analyses.

Keywords
Pine resin, Turpentine; Rosin; *Pinus caribaea* var. *hondurensis*; TGA

Introduction

Conifers can express many biochemical defense mechanisms and are enhanced following insect and microbial challenges [1-5]. In Brazil, the conifers of the Pinus species demonstrate fast growing characteristics and have good production of the wood, cellulose and resin [6]. The *Pinus caribaea* var. *hondurensis* species has origins in regions of Central America and it is genus Pinus species are also planted worldwide. However, its resin quality is few emphasized in the writings. As this species is economically important to tropical regions of Brazil, the further development of technical of resin quality analysis should be prioritized.

The resin has a complex mixture of monoterpenes and sesquiterpenes, volatile with non-volatile diterpenic acids [7]. The characteristics of resin can be sticky and liquid or brittle and solid [8]. It is an inflammable liquid secreted from epithelial cellules of the conifers [9]. It has two major fractions: turpentine, which is the volatile fraction, and rosin, which is the solid fraction [10-12]. About 95% of the total turpentine and extracted with distillation, 170ºC, while preserving its constituents [10].

Turpentine is transparent and its derivatives can be used by different industries, including pharmaceutical, cosmetic, and food industries. Its derivatives are also used by the chemical industry in the manufacturing of various products, such as paint, varnishes, adhesives, insecticides, and disinfectants [13]. Rosin is the non-volatile fraction of the resin of pines, and is composed by approximately 90% of abietic and pimaric acids [14,15]. This fraction can be used in industries paints, varnishes, plastics, lubricants, germicides, paper, cosmetics, asphalt, adhesives and pesticides [6,8,16].

The thermogravimetry analysis (TGA) is a convenient and most often used method to evaluate the thermal stability and degradation properties and behaviors of matter. Nevertheless, studies using thermal analysis in resins are limited. In tests of the use the resin material (after the mixing with the diesel fuel) show the profile of the thermal behaviors of the resin [17]. Another work [18,19] analyze the rosin-based by TGA and identified similar characteristics.

The aim of this work was to obtain a fast and precise method for quantification volatile and non-volatile fractions of resin of *Pinus caribaea* var. *hondurensis* progenies. In this manner we were able to investigate the thermal stability of the resins using the thermogravimetry analysis (TGA). These results were compared with the quantification of the volatile and non-volatile fractions obtained through evaporation of volatile compound at 170 ºC.

Materials and Methods

Origin of the resin

The resin of *Pinus caribaea* var. *hondurensis* was obtained from twenty half-sib progenies of seed orchard, located at 20º20'S and 51º23'W in Ilha Solteira municipality of São Paulo state, Brazil. The resin extraction used the American method, a chemical stimulating paste containing sulfuric acid (20%) and CEPA (2-chloroethylphosphonic acid) (3.5–4.0%) in its formulation and was applied on the sapwood or cambium surfaces [20]. The samples were saved in a dry place and away from the solar radiation.

Quantification of non-volatile fraction

The non-volatile fractions of resin were obtained through the evaporation of volatile fraction of approximately twenty grams of resin, using an analytical balance Shimadzu model AY220 with 1.10^{-4} g of precision. These analyzes were done using an oven with temperature set at 170 ºC. Because of non-volatile mass to the total mass ratios added it was possible to obtain the non-volatile fraction. The differences calculated the volatile fraction of resin.

Thermogravimetric study (TGA)

The TGA curves were obtained using a thermal analysis system (Shimadzu, DTG-60H model); the samples were heated from 30 ºC to 600 ºC using open aluminum crucibles with approximately 8 mg of the homogenized sample under a nitrogen flow of 20 $mL.min^{-1}$ at a heating rate of 5 ºC min^{-1}. The analyzes were made in duplicate. The instrument was preliminarily calibrated with standard weight and with standard calcium oxalate monohydrate. All mass loss percentages were determined using TA-60 WS data analysis software.

Results and Discussion

The average resin production of seed orchard was 4.790 kg, ranging from 0.780 gr to 16.143 kg. The correlation between the resin production and the diameter at breast height was positive and not significant (0.20). Vast possibilities exist to further enhance resin production in Brazil through the use of proper selection and breeding programs; in addition to improvements in extraction and processing techniques [21].

The evaporation of the resins in the oven with temperature set at 170 ºC can determinate the non-volatile and volatile fractions, Table 1. This temperature was chosen in order to obtain turpentine according to industrial process, extracting about 95% while preserving its constituents.

An example of TGA and DTG curves, Figure 1, show a profile of mass lost events. The DTG curve shows events observed of water lost (a), and volatile organic fraction (b). TGA curves were similar the obtained by Tsanaktsidis et al [17] to resin of the *Pinus halepensis* and rosin by Donato et al [18]. With TGA to the curve can be calculated to determine the volatile fraction of samples.

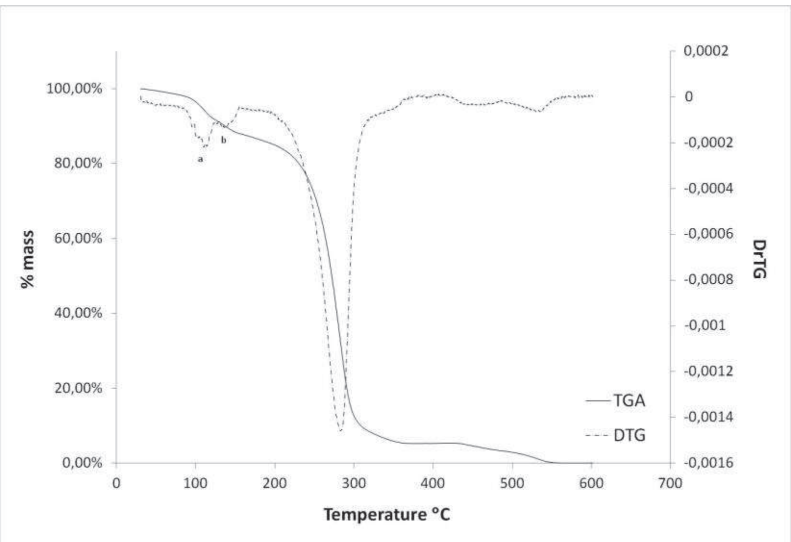

Figure 1. TGA and DTG curves of the sample 2. The events (a) and (b) represent the water and volatile organic fractions lost, respectively.

Table 1 – Non-volatile and volatile results of the samples obtained through evaporation of resin in the oven with temperature set at 170 ºC. Volatile results of the samples obtained in the TGA, analysis in duplicate, standard deviation and variation coefficients of this analysis.

Sample	Production (Kg/tree.year)	Oven		Thermogravimetry analysis (TGA)		
		Non-volatile (%)	Volatile (%)	Volatile (%)	Standard Deviations (%)	Variation Coeficients (%)
1	9.274	83.53	16.47	16.38	0.50	3.05
2	8.526	85.31	14.69	13.37	0.05	0.38
3	9.700	82.94	17.06	15.73	0.96	6.09
4	7.278	75.95	24.05	23.64	1.62	6.86
5	9.516	77.65	22.35	22.64	1.39	6.14
6	9.335	80.37	19.64	19.91	0.92	4.61
7	8.368	79.26	20.74	19.03	0.53	2.78
8	8.745	79.79	20.21	19.68	0.07	0.38
9	8.759	82.41	17.59	21.89	0.75	3.40
10	11.969	80.64	19.36	20.60	0.17	0.83
11	7.624	84.77	15.23	20.03	1.35	6.72
12	8.304	82.09	17.91	16.87	0.73	4.34
13	6.290	82.33	17.67	16.28	0.04	0.27
14	8.451	78.14	21.86	19.80	0.90	4.56
15	7.178	81.72	18.28	16.36	1.29	7.86
16	9.293	84.42	15.58	15.78	0.38	2.44
17	9.924	77.36	22.64	21.18	1.00	4.73
18	11.125	77.16	22.84	16.98	1.28	7.52
19	11.638	78.02	21.98	17.89	0.76	4.22
20	8.376	80.32	19.68	16.66	0.14	0.84
Average	8.98	80.71	19.29	18.54		
Standard Deviations	1.44	2.77	2.77	2.70		

The averages of non-volatile and volatile fractions were 80.71% and 19.29%, respectively. The highest value of volatile fractions is 24.05% and the lowest is 14.69%. The same samples were analyzed by TGA, considering the temperature range from 30º to 170ºC, and the averages of volatile fractions were 18.54%, Table 1. The highest value of volatile fractions is 23.64% and the lowest is 13.37%. These results demonstrated that TGA technique is capable of accurately determining the volatile and non-volatile fractions of the resin, unpublished results in the literature. The determination of the fractions of the resin by TGA will allow faster and more accurate analysis of quality resin.

Conclusions

The use of TGA to determination of the fractions of the resin will allow faster and more accurate analysis of quality resin. TGA technique is capable of accurately determining the volatile and non-volatile fractions of the resin. This technical proved to be suitable for further analyses.

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