Ee-JRIF

Ethiopian e-Journal
for Research and Innovation Foresight

*Ee-JRIF Vol 3, No 1 2011 – Agriculture and Forestry issue: pp (38 – 48)*

# Analysis of resin and turpentine oil constituents of *Pinus patula* grown in Ethiopia

**T. Teshome [1]**

## Abstract:

The turpentine oil of *Pinus patula* grown in Wondo Genet was obtained by steam distillation and analyzed by GC/MS. The main components found were *β*-phellandrene (43.2 %), α-pinene (19.24%), camphene and *β*-pinene (each 1.8%) and other constituents (34.0%). The chemical composition of the oil was very different from the typical oil of *Pinus radiata* with very high *β*-pinene (45%) α-pinene (39%). Waller-Duncan k – ratio t test and Duncan's Multiple Range Test revealed that mean resin and turpentine oil contents were significantly different among the age groups and diameter classes that were investigated.. The highest resin production was recorded in September for all age groups. Trees of ages 15 and 20 years produced the highest resin content in the diameter classes (25-30 cm) when compared to trees of age 13 years, which yielded high resin in the smallest diameter class (15-20 cm). The highest turpentine oil production was recorded in October. All trees falling in age groups 13 and 15 years produced the highest turpentine oil in the diameter class 20-25 cm, while trees of age 20 years produced the highest turpentine oil in the diameter class 25-30 cm. The results obtained showed that rainfall has no effect on resin production, while temperature-showed positive effect on resin production ( $p = 0.008$).

***Keywords***: *Turpentine oil, Resin, Rainfall,Temperature, Pinus patula, Pinaceae*

[1]Higher Education Relevance and Quality Agency, P.O.Box 27424/1000, Addis Ababa, Ethiopia; Email: henos_tesfaye@yahoo.com

## Introduction

*Pinus species (Fam. Pinaceae)* are one of the most widely scattered tree species in the northern hemisphere, extending from Polar Regions to the Tropics (Wormald 1975). Among pine species *Pinus patula* and *P. radiata* are widely planted exotic species in Africa. *P. patula* and *P. radiata* are also commonly planted exotic species in Ethiopia for timber and pulp production, although their use extends to resin production in Kenya and other parts of Africa. Resin extraction from pine species is not a common practice in Ethiopia, even though it is well known that the resin/oleoresin yields two industrially valuable chemical products namely the essential oil also known as oil of turpentine, and a non-volatile product, termed as rosin.

More than 100 -*Pinus* species are known to exist; only very few are tapped commercially as a source of resin (Coppen and Hone, 1995). Among the major species tapped for resin are *P. elliottii* Engelm. (Brazil, Argentina, S. Africa, USA, Kenya), -*P. massoniana* and *P. kesiya* Royale ex Gordon (China*), P. pinaster* Aiton (Portugal), -*P. merkusii* Jungh. and Vriese (Indonesia and Viet Nam), *P. roxburghii* Sarg. (India and Pakistan), *P. oocarp* Schilde (Mexico and Hondorans), *P. caribaea* (S. Africa, Kenya, Venezuela), *P. radiata* (Kenya). The relative merits of different pine species for tapping, resin yields and turpentine quality (chemical composition) varies markedly within a species, and according to provenance origin.

Turpentine is a mixture of constituents. The type and amount of specific constituents is dependent on the type of pine trees, the geographical location of the trees and the season of the harvest. For instance, as reported by Gscheidmeier and Fleig, 1996, and further cited by Scott 2002, the major constituents of turpentine produced in Greece were primarily α-pinene (92-97%), with varying amounts of β-pinene (1-3%). In contrast, Indian gum turpentine has a comparatively low α-pinene (20-40%) and a high β-pinene (5-20%).

Turpentine oil is widely used and can be applicable as a solvent in paint; varnish and boot polish industries, in pharmaceuticals as enema and in perfumery soaps, and in making synthetic camphor and pine oil by fractionating the natural products, as insecticides, disinfectants, and denaturants (Greenhalgh 1982). The major components of these natural chemicals are used as starting materials for the synthesis of a wide range of fragrances; flavors, vitamins and polyterpene resins, and can also form the basis for growing chemical industries and contributing to the domestic economy.

The turpentine industry has become one of the major sources of raw materials to organic chemicals. This is remarkable, because, turpentine is a natural product that can easily be obtained from living pine trees with out killing the trees and degrading the environment. However, the technologies are not, abundant in Ethiopia, particularly, to re-fractionate and test resin and its derivatives. Resin and turpentine oil and their derivatives have wider industrial uses in some of the Ethiopian industries, such as Equatorial (Dill) Paint Factory, Nefas Silk Paint Factory, Alkyd Resin Factory, Ethiopian Pesticide Agency (Factory) and Ethiopian Rubber and Plastic Factory and KADISCO. In this regard the Addis Ababa University (AAU) as Africa center for essential oil research supported by United Nation Industrial Development

Organization (UNIDO) has made substantial contribution in the documentation of the chemistry of the essential oils of several species (e.g. *Pinus radiata* and several *Eucalyptus* species) in Ethiopia and Africa.

Although relevant studies on resin tapping, collection, extraction, chemical analysis, applicability and standardization have been carried out in different parts of the world and compiled by Coppen and Hone (1995), little effort has been made to assess and document the production of resin and turpentine oil of pine species in Ethiopia. Considering future soap, detergent and paint chemical industries in the country, information on resin and turpentine oil production potential of *P. patula* is useful for the industrial sector to explore the feasibility of investment in launching *P. patula* or other pine species plantations in the future..

Thus, this study focuses on investigation of the resin producing capacity of *P. patula* trees by measuring the quantitative and chemical yields of turpentine oil and by assessing the influence of rainfall, temperature, size (diameter at breast height) and age of individual tapped trees on resin and turpentine oil production.

## METHOD

### Study site

The study was conducted in the *Pinus patula* stands of Wondo Genet College of Forestry. It is situated 264 Km. south of Addis Ababa. The elevation at the college varies between 1800 – 2100 m.a.s.l. The mean annual rainfall is 1163 mm. The mean monthly temperature is $19^0$C. The rainfall and temperature pattern of Wondo Genet College of Forestry where the study site is located is presented in Figure 1.

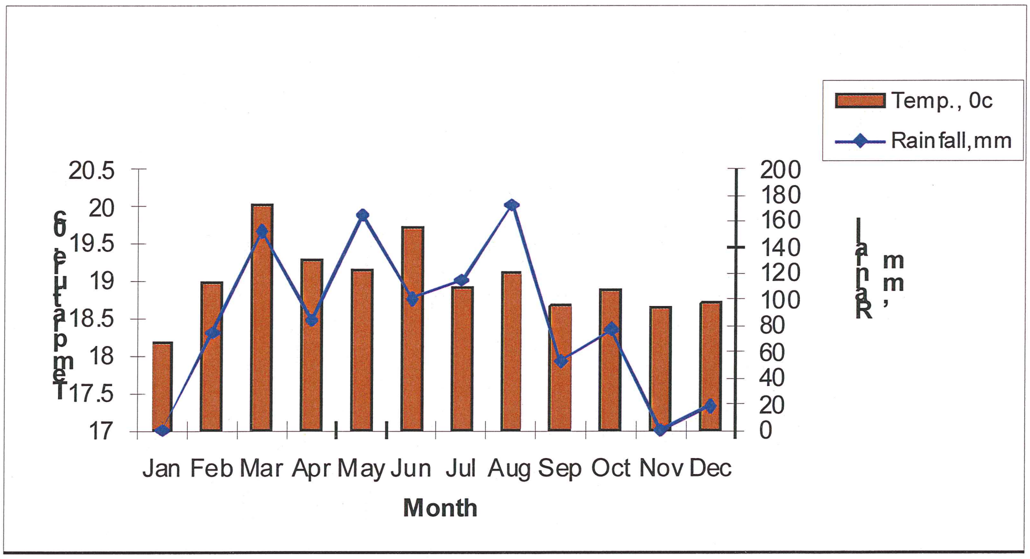



**Figure 1. Average annual rainfall and temperature of the study site in Wondo Genet College of Forestry (2001 & 2002).**

The original vegetation of the area was destroyed long ago as a result of clearance for cultivation and logging. The natural forest is now confined largely to the upper slopes. The major species constituents of the remaining natural forest in the college are: *Celtis africana, Cordia africana, Aningeria adolfi-fredrichi, Podocarpus falcatus, Milletia ferruginea, Croton macrostachys* and *Albizia gummifera*. Since the inception of the college, a great deal of effort has been made to establish plantation. Currently the college has about 100 ha of man-made forest. The major species predominantly planted is *Cupressus lustianica* followed by *Gravilla robusta* and *Pinus patula*.

**Sampling Design and Methods of Analysis**

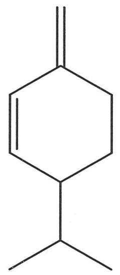
A total of 99 sample trees were marked for resin collection. The sample trees were distributed equally. There were 33 sample trees in each age group and then each age group further subdivided into 11 trees in three diameter classes in the *P. patula* stands of the college. They all were numbered to identify each single tree to record its monthly resin production. The diameters at breast height of all sampled trees were measured to assess the effect of size on resin production capacity of the species. The resin was collected by wounding or tapping the barks of pine trees carefully using sharp knife, so that the crude exude will be dropped in the receivers/cups hung just below the wounded area. Collection was done every month for 17 months to get reliable data and look into the effect of monthly rainfall and temperature on the resin production of the species. The resin produced each month was weighed and leveled for further separation of the components. The separation of the resin into its component parts, rosin and turpentine, involves two basic operations: cleaning and distillation. Cleaning is necessary to remove all extraneous material from the resin, both solid and soluble, such as forest debris (bark, pine needles). The cleaned resin was then distilled using a universally accepted steam-distillation method.

GC was performed on HP 6890 GC series using HP-5 fused silica capillary column (30 m x 0.25 mm i.d.). The oven was programmed at 50-210 $^0$C at a rate of $3^0$/min using $N_2$ as carrier gas; injector and detector (FID) temperatures were 220 $^0$C and 270 $^0$C, respectively. GC-MS were performed on Fisons GC model 8000 series chromatograph and a Hewlett-Packard GCD system coupled to MD 800 quadrupole analyzer mass spectrometer at 70 eV. The capillary column types were DB-17 (30 m x 0.25 mm i.d.) and Innowax FSC column (60m x 0.25 mm with 0.25 micrometer film thickness) and GC parameters were the same as above. The injector temperature was kept at $250^0$C. The constituents were identified by matching their 70eV mass spectra with NIST, Wiley databases and user generated mass spectral libraries. The identification of the constituents was further confirmed by comparison with GC retention times of some authentic samples.

## Results and discussion

### Chemical Analysis

Based on samples taken from three age groups and diameter classes, the major component was found to be β-phellandrene with of 43.2% (v/w) yield, followed by α-pinene (19.2%; w/v), camphere and β-pinene each constituting ca. 1.7%, and others accounting for 34.0% of the total chemical constituents. The structure of the major compound is presented in Figure 2.



β–phellandrene

**Figure 2. Structure of the major compound (β-phellandrene)**

The above results were also confirmed by C-13 NMR measurements. Moreover, the C-13 NMR spectrum also showed the presence of slight amount of limonene, which has retention time similar to β – phellandrene.

Compared to *P. patula*, the essential oil of *P. radiata* planted in Wondo Genet is composed of β-pinene (44.5%) and β-pinene (38.6%) as major constituents (Dagne et al., 1999). The quality of turpentine oil in *P. radiata*, is superior as measured by its total pinene content (95%) (Coppen and Hone 1995). In light of the above quality criteria, the turpentine oil of *P. patula* is poor in quality. The distillation of the oleoresins tapped from three P. species (*P. carbaea* var. hondurensis Barrett et Gplfari, *P. merrkusii* and *P. insularis*) at several plantations in peninsular Malaysia yielded turpentine oil in the range of 25–39 % (v/w) (Jantan and Ahmed 1999), compared to a yield of 3 – 9 % (v/w) in *P. patula* obtained in this study. This shows that *P. patula* is low quality turpentine oil-yielding pine species.

**Yield comparison**

**Resin**

Figure 3, 4, and 5 present the overall resin produced over the study period.

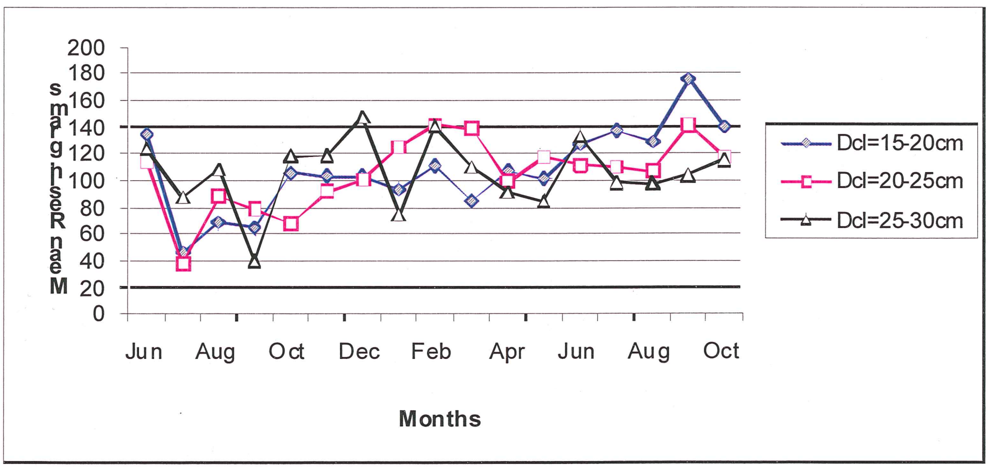



**Figure 3. Mean Resin content of *P. patula* for age 13 (n=33) and three diameter classes of 11 trees each observed during the study period**

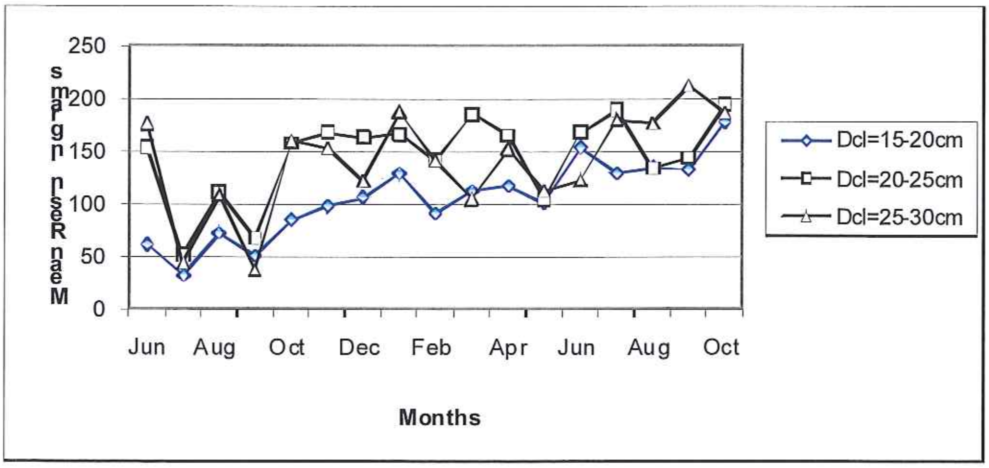



**Figure 4. Mean Resin production capacity of *P. patula* for age 15 (n=33) and three diameter classes of 11 trees each observed during the study period**

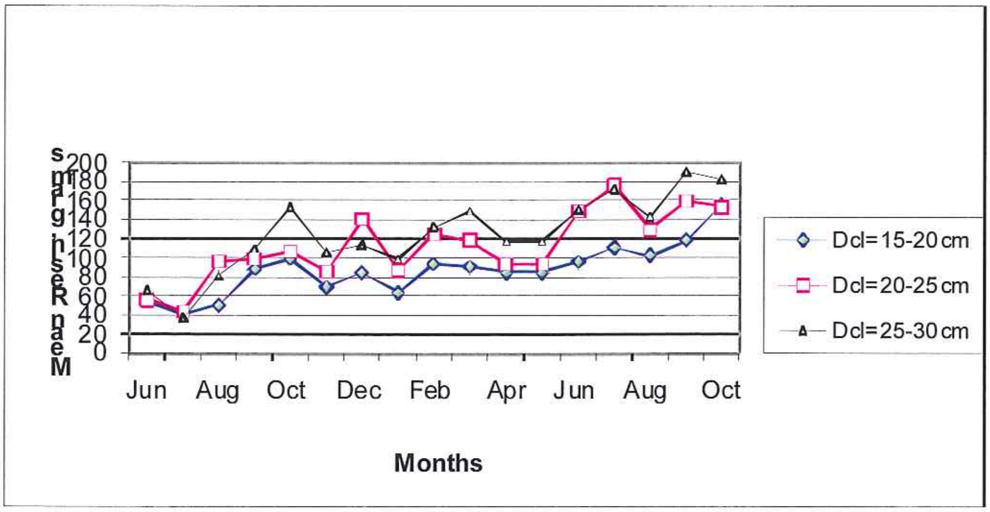



**Figure 5. Resin production capacity of *P. patula* for age 20 (n=33)**

The highest resin production was recorded in September for all age groups. The resin production capacity, however, differs from diameter class to diameter class. Trees of age 15 and 20 produced the highest resin in the diameter classes (25-30 cm), when compared to trees of age 13, which yielded high resin in the smallest diameter class (15-20 cm).

The influence of age, size (diameter at breast height), temperature and rainfall on the resin production capacity of *Pinus patula* was further examined using a statistical package SAS 1994. The ANOVA procedure used was the Waller-Dunkan K-ratio t-test and Duncan Multiple Range Test to analyze the mean values of resin for different age groups and diameter classes. The overall F test was found significant, indicating that the model (resin) as a whole accounts for a significant proportion of variability in the resin production. The F test for the diameter and age groups was also significant, indicating that the means of resin contents for the different age and diameter classes are not all equal. From these tests (Waller-Duncan k – ratio t-test and Duncan's Multiple Range Test) one concludes that the mean resin content for the three diameter classes (Figure 6) for age group 15 (129.72 gm) is higher than the mean for age group 13 (108.34 gm) and age group 20 (106.35 gm) respectively. Likewise, the average resin content of diameter class 25-30 cm (123.28 gm) is higher than the averages for diameter class 20-25 cm (120.95 gm) and diameter class 15 – 20 cm (100.20 gm).

A pair-wise t-test (Least Significant Difference, LSD) revealed no significant mean differences between age 13 and 20 P >0.05). Differences between all other means of resin content in the rest of the age groups compared were significant P<0.05 Correspondingly, there was no significant difference noticed between diameter classes of 20-25 and 25-30 cm. P>0.05 The fact that rainfall is a continuous variable and an interaction of rainfall and resin production is sought, a GLM (General linear model) test was undertaken to check the effect of rainfall on resin production. The result showed that rainfall has no effect on resin production, while temperature showed positive effect on resin production P>0.05

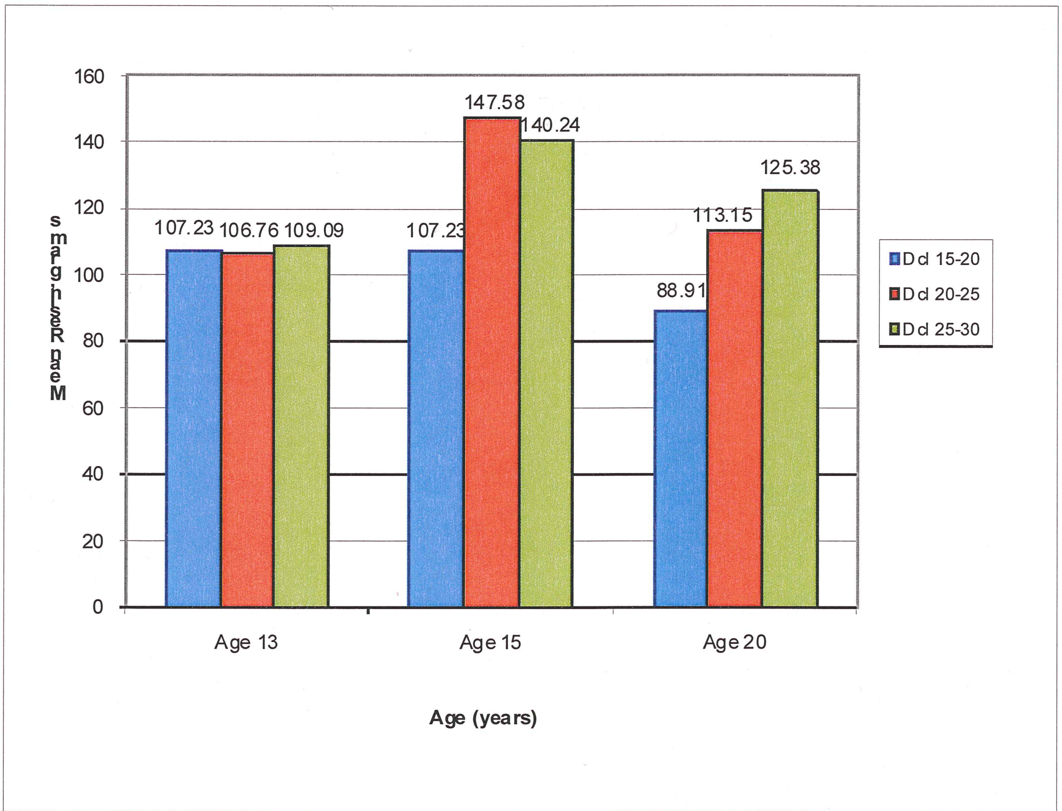



**Figure 6. Comparison of mean values of resin content for the three age groups and diameter classes of *P. patula***

**Turpentine oil extracts**

Figures 7, 8, and 9 present the overall turpentine oil produced during the study period. The highest turpentine oil production was recorded in October (the mean of each diameter group combined in each age group). All trees falling in age group of 13 and 15 produced the highest turpentine oil in the diameter class 20-25 cm, while trees of age 20 produced the highest turpentine oil in the diameter class 25-30 cm.

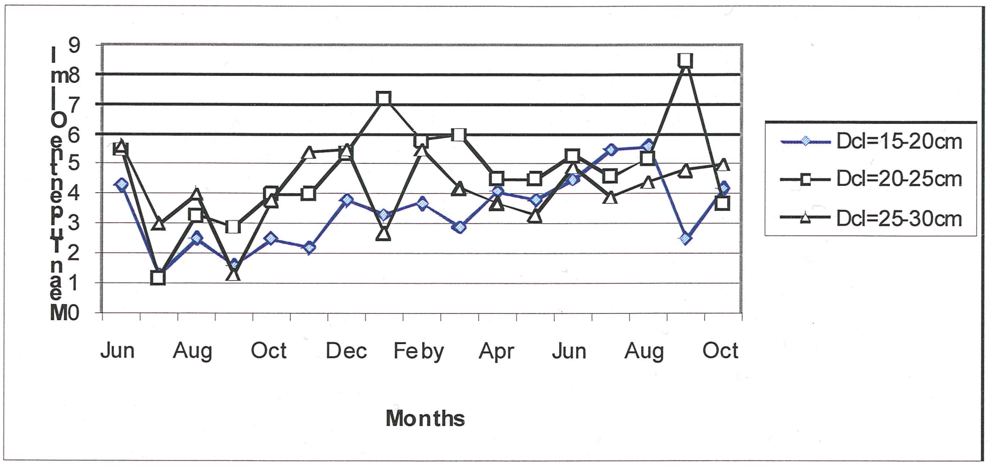



**Figure 7. Comparison of mean values of turpentine oil in *P. patula* for age 13 and three diameter classes observed during the study period**

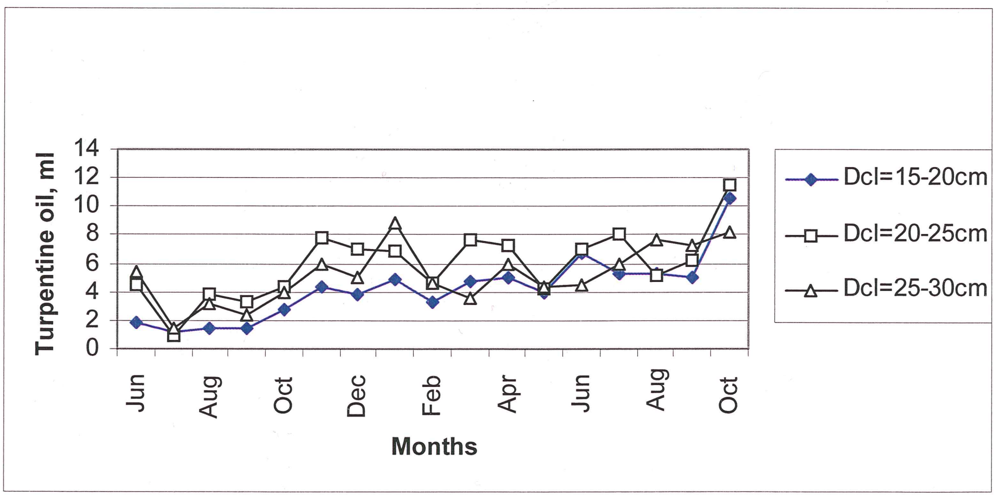



**Figure 8. Comparison of mean values of turpentine oil of *P. patula* for age 15 and three diameter classes during the study period**

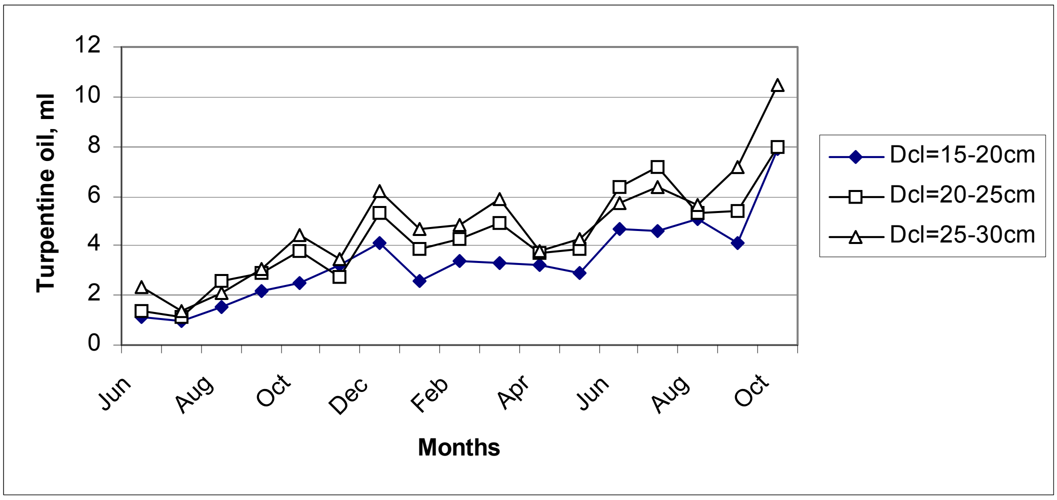



**Figure 9. Comparison of mean values of turpentine oil in *P. patula* for age 20 and three different diameter classes during the study period**

The turpentine oil yield was analyzed using a statistical package SAS 1994. The ANOVA procedure used was the Waller-Dunkan K-ratio t-test and Duncan, Multiple Range to test the equality of the mean values for different age groups and diameter classes. The results showed that the overall F test are significant, indicating that the model as a whole accounts for a significant portion of the variability in the turpentine oil yield. The F test showed the means of the turpentine oil for the different age and diameter groups are not equal. The mean turpentine oil content (Figure 10) for the age group 15 (5.10 ml) is higher than the means of the age group 13 (4.15 ml) and age group 20 (4.13 ml). Correspondingly, the mean turpentine oil of diameter class 20-25 cm (4.99 ml) is higher than the means of diameter class of 25-30 cm (4.72 ml) and diameter class of 15-20 cm (3.67 ml).

The turpentine oil yield comparison among three age groups depicted that there are significant differences between all means except between age class 13 and 20. The content of turpentine oil in each showed no significant differences between diameter classes of 20-25 and 25-30 cm when compared to those in all other diameter classes. Two (age 13 and 20) of the tests showed the same results.

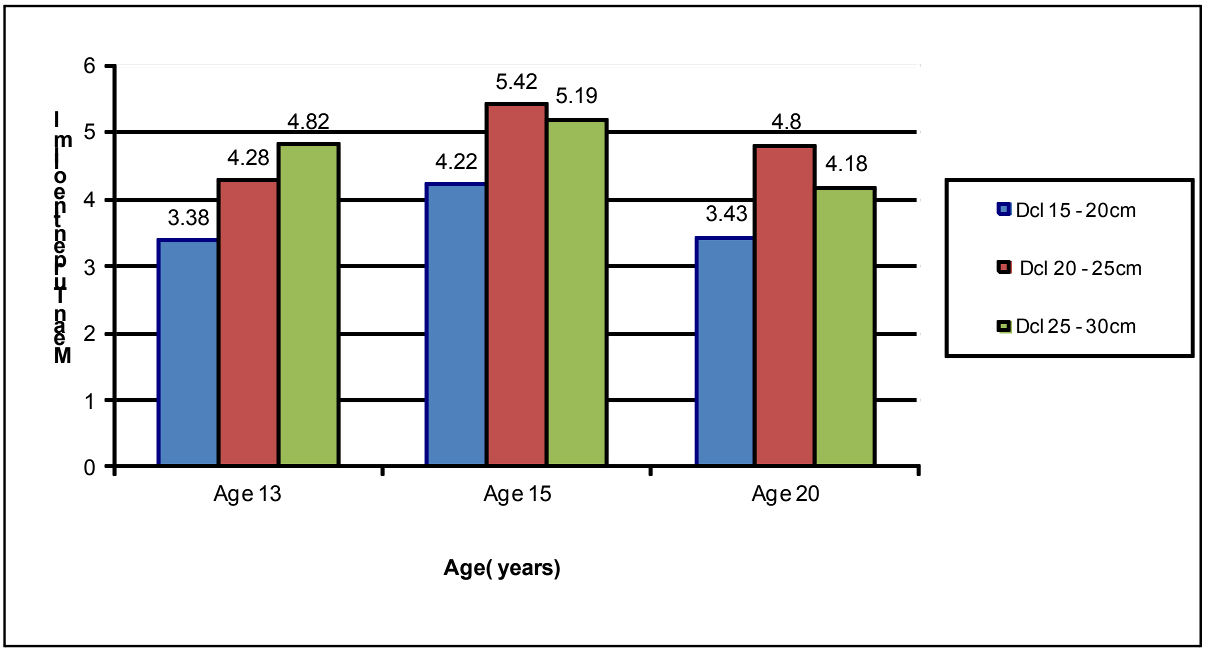



**Figure 10. Comparison of average turpentine oil yield for three diameter and age groups of *P. patula.***

**Rosin**

Rosin is the major product obtained from pine resin. It remains behind as the involatile residue after distillation of the turpentine and is a brittle, transparent, and glassy solid. It is insoluble in water, but soluble in many organic solvents. It is graded and sold on the basis of color, the palest shades of yellow-brown being the better quality. Their most important uses are in the manufacture of adhesives, paper sizing agents, printing inks, solders and fluxes, various surface coatings, insulating materials for the electronics industry, synthetic rubber, chewing gums and soaps and detergents.

The determination of the chemical properties and weight proportion of rosin were not investigated in this study.. However, the weight of rosin produced from distillation of a given quantity of resin can be easily estimated from past experience. Most distillation of resin often produces gum rosin and gum turpentine in varying ratios, usually between 4:1 and 6:1 as reported by Coppen and Hone (1995). In light of this international experience, the total amount of rosin produced from any given amount of *P. patula* resin distilled could be approximated in the range of 80 – 85%.

**Summary**

The highest resin production was recorded in September for all age groups. The findings of this study showed that resin production capacity of *P. patula* differs from diameter class to diameter class. The average resin content of diameter class 25-30 cm is higher than the averages for diameter class 20-25 cm and 15 – 20 cm. This result confirms that the greater the diameter of the tree tapped and the bigger the proportion of live crown, the greater the resin yields as reported by (Coppen and Hone 1995). The mean resin content for age group 15 is higher than the averages for age group 13 and 20.

The highest turpentine oil production was recorded in October for all trees falling in age group of 15 followed by age group 20 as opposed to trees of age 13 which produced least. No significant differences observed between all turpentine oil produced among three age groups except averages between age class 13 and 20. Comparison of turpentine oil production between diameter classes showed no significant differences between diameter classes of 20-25 and 25-30 cm, when compared to all other average values in all other diameter classes. Rainfall showed no effect on resin production as opposed to temperature, which revealed positive effect on resin production ($P = 0.008$).

The major chemical constituents of turpentine oil of *P. patula* are β-phellandrene with percentage value (v/w) of 43.2, followed by α-pinene (19.2%), camphere and β-pinene constitute ca. 1.7% each and others contributing to 34.0%. The high proportion of β-phellandrene and low constituents of α-pinene makes the turpentine oil of *P. patula* poor quality. These findings warrant interested investors in this area to look for other pine species for quality turpentine oil.

While most pines are capable of yielding resin on tapping, it is only economic to do so if the quantity obtained is sufficient and its quality is acceptable. Both these factors are determined primarily by the species of *Pinus*, which is tapped, so information made available in this study provides an insight on the suitability of *P. patula* for gum naval stores production. The average resin yield of *P. patula* observed in this study (1.5kg/tree/year) makes *P. patula* uneconomical to support gum naval stores. Hence, pine species such as *P. elliottii* and *P. caribaea* var. *caribaea* (South Africa) and *P. caribaea* var. *hondurensis* from Kenya could be considered as potential high quality resin producing pine species in Ethiopia. Considering future soap, detergent, perfumery, paint and pulp industries in Ethiopia, establishment of pine plantation with suitable type for resin production is an economically and environmentally justified investment .

## Acknowledgement

I gratefully acknowledge the Ethiopian Science and Technology Commission for providing me the fund to run the project. Special thanks go to Professor Ermias Dagne, Addis Ababa University

Chemistry Department, for his support in analyzing and determining the content of the turpentine oil of *Pinus patula*. I appreciate and thank Mr. Taye Gidyelew and Mr. Mulugeta Badasa for their time and contribution in data collection and steam distillation of the sample data.

**REFERENCES**


Coppen, J.J.W. and G.A. Hone. 1995. Gum naval stores: turpentine and rosin from pine resin. FAO, Non-wood Forest Products No. 2, 62 pp.

Ermias Dagne, Tefera Bekele, Daniel Besrat, Markos Alemayehu, Tadele Worku and J.P. Elokaokich. 1999. Essential oils of resins from three Pinus species growing in Ethiopia and Uganda. SINET, 22(2):253-257.

Greenhalgh, P. 1982. Production, marketing and utilization of naval stores. Tropical Products Institute. London.

Jantan, I. and A. S. Ahmad. 1999. Oleoresin of three pine species from Malaysia pine plantations. Asian Review of Biodiversity and Environmental Conservation. 9 pp.

Masten, S. 2002. Turpentine (Turpentine oil, wood turpentine, sulfate turpentine, sulfite turpentine): Review of toxicological literature. National Institute of Environmental Health Sciences. North Carolina.

SAS. 1994. SAS/STAT User's guide. Version 6, 4$^{th}$ edition, Vol. 2, SAS Institute Inc.1673 pp.

Wormald, T.J. 1975. *Pinus patula*, Tropical Forestry, Pap. No. 7, Dept of Forestry, Commonwealth Forestry Inst., University of Oxford England.