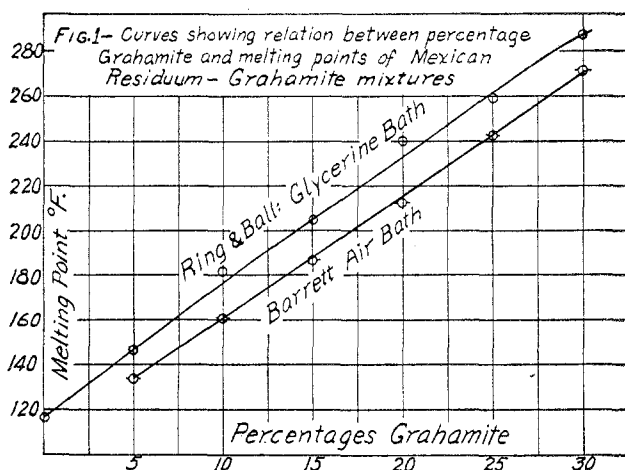


TABLE II—PRODUCTS OBTAINED BY FLUXING GRAHAMITE WITH MEXICAN RESIDUUM

MATERIALS AND MIXTURES	PER CENT		MELTING POINT °F.			CHARACTER OF PRODUCT	
	Fixed Carbon	Ash	Ring and Ball Water	Barrett Glycerine	Air		
M Mexican residuum	17.26	tr.	104.7	117.3	Too soft	Semi-fluid	
R 485° F. 20 hr. residue	21.22	0.04	hard	191.5	179.0	Too	Tough
Per cent % loss on M. Gr. fluxing							
A 95 5	130.3	145.4	133.0	Soft Homogeneous	
B 90 10 ..	20.34	0.08	..	181.4	162.0		
C 85 15 2.15	212.0	187.0	Homogeneous	
D 80 20 1.90	22.72	0.24	Too hard	238.3	229.0	Homogeneous	
E 75 25 1.15		257.0	241.0	Homogeneous	
F 70 30 1.25	26.62	0.24	..	288.0	269.0	Fairly homogeneous. Brittle	

$\frac{3}{8}$ in. in diameter and weighing $3\frac{1}{2}$ g. is placed on top of the sample which is then suspended in a 600 cc. beaker containing 400 cc. of glycerine, the bottom of the cylinder being 1 in. from the bottom of the beaker. A thermometer is suspended in the bath with the bottom of the bulb flush with the bottom of the cylinder. The bath is heated at the rate of 7° C. per minute with constant stirring. The temperature registered at the time the sample touches the bottom of the beaker is recorded as the melting point of the material. The rate of heating exercises a marked effect on the melting point and must be watched closely to obtain concordant results.

The reflux solubilities and the air melting points were made as described by S. R. Church.¹ The various other tests noted were made according to the methods



recommended by Prevost Hubbard² and by Clifford Richardson.³

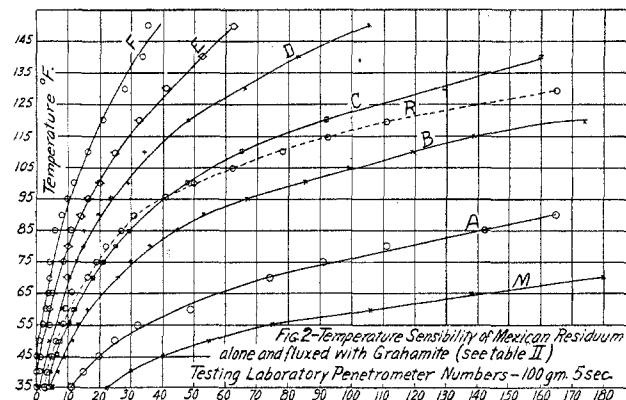
CONCLUSIONS

I—Fig. 1 shows a fairly regular increase of melting points of the fluxed products with increasing percentages of the asphaltite.

II—It is of interest to note in Fig. 2, that the temperature-penetration curve of the residue from a 485° F.—20 hour evaporation test of the original residuum follows very closely the curve given by the sample containing 15 per cent of the asphaltite.

III—The writer believes that too much emphasis is often placed on the melting point of an asphaltic

material or on the penetration at one specified temperature. The flattening out of the temperature-penetration curves far below the so-called melting points emphasizes this point. A series of determinations plotted as in Fig. 2 may be of assistance in many



cases in predetermining and comparing the values of new "mixes."

NOTE—The writer is indebted to Mr. S. Drucker for the preparation of the graphs which accompany this article.

TECHNICAL DEPARTMENT, MORRIS AND COMPANY
UNION STOCK YARDS, CHICAGO

INVESTIGATIONS ON THE OIL OF EUCALYPTUS GLOBULUS OF CALIFORNIA

By CHARLES E. BURKE AND CHARLES C. SCALIONE

Received December 21, 1914

For many years considerable interest has been taken in California, in the *Eucalyptus globulus* (Blue gum), a tree which, while a native of Australia, has been transplanted and thrives well on many parts of the Pacific Coast. The fact that the tree grows very fast, and yields a hard wood makes it a tree particularly desirable in these localities which are almost destitute of hard woods.

Many difficulties have been met in seasoning the wood which has a great tendency to warp and check, but these have been largely overcome by experienced lumbermen and it is now easily possible with certain precautions to prepare from the *Eucalyptus* a good clean lumber, which for hardness and tensile strength compares very favorably with oak or hickory.

In Australia one of the valuable products of the tree has been the oil which is obtained by the distillation of the leaves; this oil finds extensive use in the arts and in medicine and is imported in large quantities annually from Australia into the United States. The United States Pharmacopeia describes the oil as:

"A colorless or pale yellow oil, having a characteristic or aromatic and somewhat camphoraceous odor, and a pungent, spicy, and cooling taste. Specific gravity, 0.905 to 0.925 at 25° C. Soluble in all proportions in alcohol; also soluble in three volumes of 70 per cent alcohol. Its alcoholic solution should be neutral to litmus. It is dextrogyrate, the angle of rotation being not more than $+10^{\circ}$ in a 100 mm. tube

¹ THIS JOURNAL, 3 (1911), 227; 5 (1913), 195.

² "Dust Preventives and Road Binders."

³ "The Modern Asphalt Pavement."

at a temperature of 25° C. If 2 cc. of the oil be mixed with 4 cc. of glacial acetic acid and 3 cc. of a saturated solution of sodium nitrite be gradually added, the mixture when gently stirred should not form crystals of phellandrene nitrite. It should become semi-solid on being stirred, when cold, with a third or a half of its volume of phosphoric acid of commerce of specific gravity 1.750 (presence of a due proportion of cineol)."

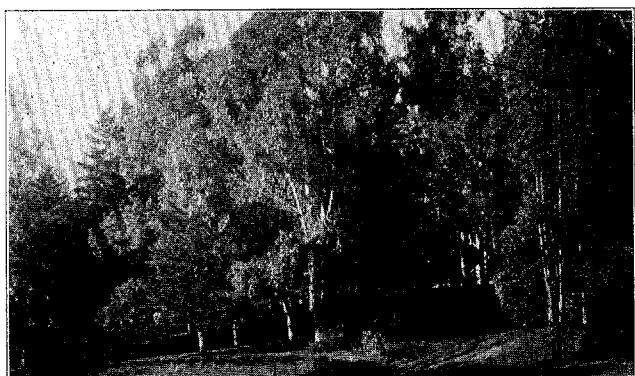


FIG. I.—EUCALYPTUS GROVE ON THE CAMPUS OF THE UNIVERSITY OF CALIFORNIA. TREES APPROXIMATELY THIRTY YEARS OLD

The Australian oil fulfils these specifications but the Californian oil does not, and therefore the latter has not been utilized to any great extent. It is this fact that has led us to an examination of the Californian oil, to determine whether there is any difference in the crude oil from the same species of *Eucalyptus* grown in Australia and California, or whether the difference is simply in the method of refining.

Baker and Smith¹ after a very extensive research on the *Eucalyptus* oils of Australia state that "the constituents of the oil of *Eucalyptus globulus* are practically constant wherever the tree is grown; a sample of oil distilled from trees in New South Wales differed in no respect from the product of trees grown in Tasmania or Victoria. The amounts of the constituents may vary but the constituents found are always the same." Our work on the Californian oil has fully corroborated this statement, since we have found exactly the same constituents in the Californian oil that Baker and Smith found in the Australian oils. The amounts of the constituents vary so greatly, however, as to give the crude oils entirely different properties. This may be seen from the following comparison of the Australian oil and Californian oil.

	CALIFORNIAN OIL	AUSTRALIAN ¹ OIL
D ₂₀	0.9052	0.913
[α] _D ²⁰	14° 42	9° 2
N _D ²⁰	1.46053	?
	Insoluble in 70 per cent alcohol	Soluble in 1.5 volumes of 70 per cent alcohol
Free acid.....	0.73	1.1
Saponification No.....	2.5	1.0
Acetylation No.....	56.0	?

These data were obtained from leaves of the *Eucalyptus globulus* gathered on the University Campus and distilled with steam at a pressure of four pounds;

¹"A Research on *Eucalyptus* with Particular Reference to Their Essential Oils," by Baker and Smith. Published by the Australian Government.

these leaves gave a total yield of oil corresponding to 0.8 per cent of the total weight of the green leaves. Baker and Smith have obtained yields as high as 0.918 per cent; this of course varies somewhat with the season of the year. For the rest of our work, since we wished to make our analysis as valuable as possible commercially, we have used oil obtained from a commercial still in North Berkeley. This oil was obtained from a grove of almost pure *Globulus* but containing a sprinkling of other varieties and would more fairly represent the average Californian oil than an absolutely pure *Globulus* oil.

This oil was fractionally distilled and the following table shows the fractions obtained with the constants of each.

Fraction No.	Temperature ° C.	Percentage oil in each	D ₂₀	N _D ²⁰	[α] _D ²⁰
1.....	85-100	3.1	0.866	1.4485	15.25
2.....	100-155	0.8	0.885	1.4606	20.11
3.....	155-165	6.5	0.887	1.4635	19.17
4.....	165-170	35.6	0.896	1.4635	16.00
5.....	170-180	30.0	0.909	1.4645	8.80
6.....	180-190	11.1	0.921	1.4675	3.81
7.....	190 up	12.5	0.980

From the curves in Fig. II it will be seen that there are at least four constituents in the oil: the first distills between 85° and 155°, the second between 155° and 170°, the third between 170 and 180, and the fourth above 180.

BUTYRIC, ISOVALERIC, AND CAPRONIC ALDEHYDES—
In the fraction boiling below 155° C. the strong irri-

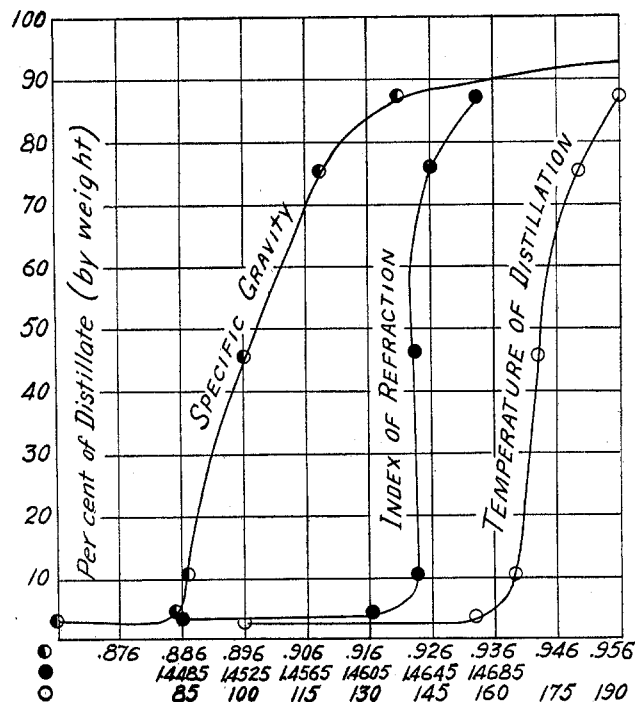


FIG. II.—BOILING POINT, SPECIFIC GRAVITY AND INDEX OF REFRACTION CURVES FOR EUCALYPTUS OIL¹

tating odor suggested the presence of aldehydes; on redistillation this part was easily divided into three fractions, the first distilling at 75-85°, the second at 85-100°, and the third at 100-140°. The first of these fractions readily formed an addition product with ammonia which after recrystallization from alcohol melted at 26-27° C. The second one also formed an

¹ See Burke and Scalione, THIS JOURNAL, 6 (1914), 804.

addition product with ammonia which after recrystallization melted at 52–53°. The first of these fractions was undoubtedly butyric aldehyde, and the second isovaleric aldehyde since the ammonia addition products of these two aldehydes melt at 29°, and 56°, respectively. The third fraction formed no addition products with ammonia but the boiling point and other physical properties indicated capronic aldehyde. A quantitative analysis of the fresh oil, by the sodium sulfite method of Sadtler and Burgess,¹ showed the total aldehyde content of the oil to be 6 per cent of the total volume.

PINENE—After the removal of the aldehydes the remainder of fractions 1, 2 and 3 was combined with fraction 4 and redistilled. The fraction distilling at 156–157° constituted approximately 20 per cent of the original volume of the oil and the following constants would seem to indicate that it was practically pure pinene.

	Distillate 156–157° C.	PURE PINENE
D ₂₀	0.878	0.8767
[α] _D ²⁰	34°	20–49°
Boiling point.....	156–157°	156–157°
Melting point nitroschloride..	102–103°	102–103°

A quantitative analysis for pinene was also made on the crude oil as follows: a weighed portion of the oil was fractionated and the fraction boiling at 130–176° retained; 5 cc. of the oil in this fraction were placed in a cassia flask and 50 per cent resorcinol solution was added to take up all the cineol and traces of aldehydes present; after the solution became clear the unabsorbed oil amounted to 21–22 per cent of the whole. This oil had the same properties as the pinene above which had been purified by distillation.

CINEOL—The remainder of the oil from the first fractions was added to fractions 5 and 6, and redistilled; after several fractionations a fraction was obtained which boiled at 176°. A comparison of the constants of this fraction with those of pure cineol shows that this fraction was cineol.

	Distillate 176–177°	PURE CINEOL
Boiling point.....	176–177°	176
D ₂₀	0.930	0.9267
N _D ²⁰	1.457	1.4559
Melting point iodol (after recrystallization) ..	111°	112°

The iodol formed from this distillate after recrystallization melted at 111°. Cineol iodol melts at 112°. A quantitative analysis by the U. S. P. phosphoric acid method gave 47 per cent cineol by volume.

EUDESMOL AND GLOBUOL—The fraction boiling at 190° and up was placed in a shallow dish and allowed to stand for several days until crystals began to separate; these were removed, dried on a porcelain plate, dissolved in alcohol and after adding enough water to produce turbidity allowed to evaporate spontaneously until crystals separated. After another recrystallization soft white flaky crystals were obtained which gave the following constants:

B. p. = 255° M. p. = 80° D₂₀ = 0.988
 [α]_D²⁰ = + 31.21° in 12 per cent chloroform solution.

Assuming the formula proposed by Semmler and

Tobias,¹ namely, a bicyclic alcohol with an unsaturated grouping, the theoretical molecular index of refraction would be 68.069; the observed molecular index of refraction was 68.001. The acetate prepared by a mixture of acetic anhydride and sodium acetate gave constants identical with those obtained by Tobias and Semmler. This and the general properties of the body seemed to indicate that we were dealing with an alcohol rather than an oxide as suggested by Baker and Smith.

In the higher boiling portions a body corresponding to globuol was separated. Semmler and Tobias consider that this body bears the same relation to eudesmol that borneol bears to isoborneol.

Considering the formulas of the two alcohols to be C₁₅H₂₆O the acetylation number would indicate that the alcohols form 23.22 per cent of the total weight of the oil.

The complete analysis shows that the oil contains the following constituents in the given percentages:

ALDEHYDES (butyric, isovaleric, and capronic).....	6
PINENE.....	21–22
CINEOL.....	47
ALCOHOLS (eudesmol, globuol, with traces of free acids and esters).....	23

In order to determine whether or not the oil from the burrs, which are necessarily gathered in large quantities with the leaves, had any detrimental effect upon the oil as a whole, a quantity of the burrs were

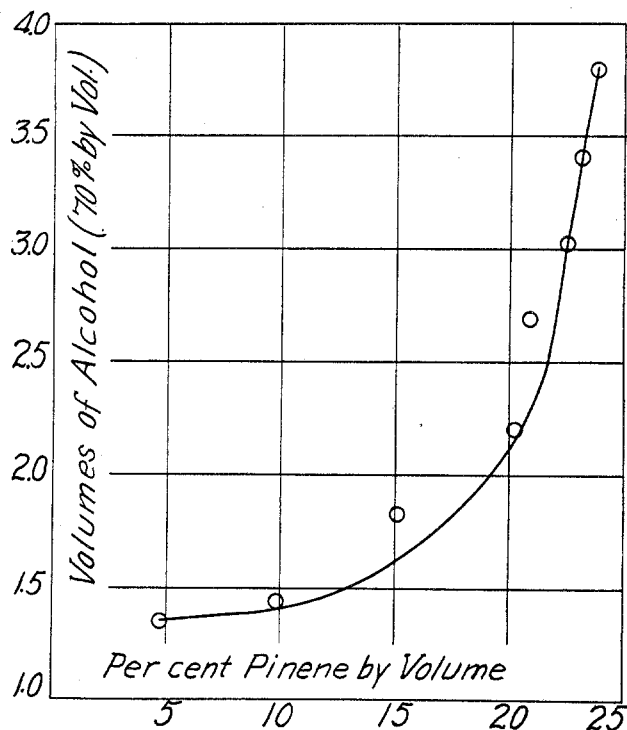


FIG. III—EFFECT OF PINENE UPON THE SOLUBILITY OF CINEOL

collected, ground and steam-distilled. The yield of oil corresponded to 0.2 per cent of the weight of the burrs. The oil thus obtained was of a lighter specific gravity and had a greater rotation than the leaf oil; it dissolved in 18 volumes of alcohol (70 per cent by weight) while the leaf oil dissolves in 15 volumes. This would seem to indicate that the burrs have a

¹ Burgess, *Analyst*, 29 (1904), 78.

¹ Semmler and Tobias, *Ber.*, 43 (2), (1913), 2026.

detrimental effect upon the oil and should be removed as far as possible.

The above analysis would seem to indicate that the chief difference between the Californian and Australian oils is in the exceedingly high content of pinene found in the Californian oil; this would account for the high rotation and low specific gravity of this oil. In order to determine the effect of the pinene upon the solubility in alcohol, pure pinene and cineol were mixed in definite proportions and the solubility in alcohol determined. Fig. III shows the effect of varying concentrations of pinene upon the solubility of cineol. It is readily seen that above certain percentages of pinene the mixture would become practically insoluble in 70 per cent alcohol.

SUMMARY

The above investigation has brought out the following facts:

I—The oil from the *Eucalyptus globulus*, from trees grown in California, has the same constituents as the oil of the Australian trees but in different proportions.

II—The reason why the Californian oil does not fulfil the U. S. P. requirements is probably due in great part to the exceptionally high pinene content.

Since Eucalyptus oil could be easily produced in large quantities in various parts of California and other Pacific coast states, a method of refining the oil so as to bring it up to the U. S. P. specifications would be particularly valuable. The investigation is being continued by the present authors with this idea in view.

CHEMICAL LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY

THE SEPARATION OF GASES BY FRACTIONAL DISTILLATION IN A VACUUM AT LOW TEMPERATURES¹

By G. A. BURRELL AND I. W. ROBERTSON

Received November 25, 1914

The authors have separated many gaseous mixtures by means of fractional distillation in a vacuum at low temperatures, and have found the method useful, accurate and applicable to a wide range of mixtures. Some of the latter are impossible to separate by other methods and some are exceedingly difficult. Hence there is presented in this paper a summary of the results so far obtained, with a discussion of the application of the method to mixtures other than those experimented with. To date three papers on the subject have been presented by the Bureau, as follows:

1—Gas analysis by fractional distillation at low temperatures.² In this paper was shown the separation of the paraffin hydrocarbons in natural gas.

2—The separation of the illuminants of mixed coal and water gas.³ In this paper was shown the method of separating the paraffin hydrocarbons, olefine hydrocarbons and benzene in mixed coal and water gas.

3—The determination of gasoline vapor in air.⁴

¹ Published by permission of the Director of the Bureau of Mines.

² J. A. C. S., 36 (1914), 1537.

³ THIS JOURNAL, 7 (1915), 17.

⁴ *Ibid.*, 7 (1915), 112.

In this paper was shown a method for separating gasoline vapor from air.

PARAFFIN HYDROCARBONS—Any combination of the gaseous hydrocarbons, methane, ethane, propane and the two butanes, can be separated by first liquefying the mixture at the temperature of liquid air, removing the methane at that temperature, the ethane at a temperature not higher than -140° C., the propane at a temperature not higher than -120° C., the butanes at a temperature not higher than -95° C. leaving the pentanes or higher paraffins as a final residue.

OLEFINE HYDROCARBONS—Any combination of the gaseous olefine hydrocarbons, ethylene, propylene, and the butylenes, can be separated. The ethylene can be removed at a temperature not higher than -140° C., the propylene at a temperature not higher than -120° C., leaving the butylenes as a residue.

PARAFFIN AND OLEFINE HYDROCARBONS—Any combination of the paraffin and olefine gaseous hydrocarbons can be separated. The methane can be removed at the temperature of liquid air. The ethane and ethylene can be removed at a temperature not higher than -140° C. The propylene and propane can be removed at a temperature not higher than -120° C., leaving the butanes and butylene as a residue. The pairs of constituents can be analyzed as such by combustion in oxygen, and from this data the percentage of each one determined. The authors have separated ethylene and ethane, boiling point only 10° C. apart, but the operation is too tedious to be of practical value.

BENZENE VAPOR in air or in mixture with other gases, such as coal gas, can be separated at the temperature of liquid carbon dioxide (-78° C.). In the case of benzene vapor and other gases that represent the final or the only separation desired in mixtures, it is most convenient to measure their pressure after the removal of the other constituents. The volume present can be calculated from this pressure. For instance in the case of benzene vapor in air or coal gas, the mixture is introduced into the liquefaction bulb at atmospheric pressure. It is then cooled by surrounding the liquefaction bulb with liquid carbon dioxide and removing as much gas as is possible with a vacuum pump. Next the stopcock on the liquefaction bulb is closed, the refrigerant removed, and the pressure of the benzene read on a manometer attached to the liquefaction bulb. If a represents the pressure of the atmosphere and b the partial pressure of the benzene vapor, the percentage of benzene by volume becomes $100 b/a$: water vapor is removed by absorbing same in phosphorus pentoxide.

GASOLINE VAPOR IN AIR—It was found necessary to adopt a temperature lower than that of liquid carbon dioxide in order to separate gasoline vapor from air, hence liquid air was used since it has to be used and time is consumed in obtaining temperatures between those of liquid carbon dioxide and liquid air. The partial pressure of the gasoline is determined in the same way as is that of the ben-