

SOME ATTEMPTS TO CRACK AND CLASSIFY
NEW BRAUNFELS CEDAR WOOD OIL

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THESIS

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Woodleigh James Champion, B. S.
(San Marcos, Texas)

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TABLE OF CONTENTS

Chapter	Page
I. INTRODUCTION.	1
A. The Problem Stated.	1
B. Why the Problem Was Chosen.	1
C. History of Related Work	2
D. Limitations	3
II. CRACKING AND THE CRACKING PROCESS	4
A. The Cracking Process.	4
1. The Commercial Cracking Process	4
2. Description of the Cracking Still Used in This Investigation.	5
B. Procedure for Cracking.	6
C. Vacuum Distillation of Oil Subjected to the Cracking Process.	7
D. Discussion of Data Tables	8
III. PHYSICAL CONSTANTS AND CHEMICAL REACTIONS	14
A. Physical Constants.	14
B. Solubility Grouping	14
1. Qualitative Analysis for Nitrogen, Sulfur and the Halogens	14
2. Grouping by Solubility.	15
C. Class Reactions	17
1. Tests for Unsaturation.	17
2. Reaction of Aldehydes and Ketones	17
3. Neutral Equivalent.	18
4. Reaction With Sodium.	18
D. Separation of a Water-Insoluble Mixture	18
E. Oxidation of the 250.2° C. Fraction	19
IV. SUMMARY	21
BIBLIOGRAPHY.	22

LIST OF TABLES

Table	Page
I.	9
II.	10
III.	11
IV.	12
V.	15
VI.	16

SOME ATTEMPTS TO CRACK AND CLASSIFY
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CHAPTER I

A. The Problem Stated

The problem of this investigation is to develop a method for cracking crude cedar wood oil and to classify the resulting products. The question of whether or not the crude cedar wood oil was cracked is to be determined by comparison of physical constants. The classification of the sample will be by class reactions. The oil used in this problem was obtained from the Southwest Texas Cedar Oil Company in New Braunfels, Texas.

B. Why the Problem Was Chosen

This problem was selected as a continuation of work begun by Shepard¹ and Phillips² on separating and identifying

¹J. C. Shepard, Partial Separation of the Constituents of Pyrolyzed Cedar Wood Tar, Unpublished Master's Thesis, (1948).

²J. N. Phillips, Chemical Reactions of the 250.8° Centigrade Fraction of Oil Pyrolyzed from Cedar Wood Tar, Unpublished Master's Thesis, (1948).

the constituents of pyrolyzed cedar wood tar.

Much of this investigation was done in collaboration with Hageman³, who has presented the cracking process used

³H. H. Hageman, Some Chemical Reactions of Cracked New Braunfels Cedar Wood Oil, Unpublished Master's Thesis, (1949).

and some chemical reactions of the oil obtained. The writer has continued research on the physical constants to establish evidence of any appreciable amount of cracking present in the oil and to classify the sample by class reactions.

C. History of Related Work

Investigations concerning the components of New Braunfels variety of cedar wood oil were begun at Southwest Texas State Teachers College by Howard Black in September, 1938, under the direction and supervision of Dr. C. L. Key. Since 1938, graduate research students have continued to investigate the chemistry of these components. Gary⁴ has surveyed

⁴C. E. Gary, A Survey of the Cedar Research Completed at Southwest Texas State Teachers College, Unpublished Master's Thesis, (1948).

graduate research done at this institution on cedar wood oil. In September, 1948, Hageman⁵ began experimentation with

⁵H. H. Hageman, op. cit., p. 3.

crude cedar wood oil to parallel work begun by Shepard⁶ and

⁶J. C. Shepard, op. cit., p. 2.

Phillips⁷ on the oil obtained from pyrolyzed New Braunfels

⁷J. N. Phillips, op. cit., p. 2.

cedar wood tar.

D. Limitations

This investigation is limited to the determination of any appreciable amount of cracking in the fraction of oil boiling at 250.2° C. obtained from the process described by Hageman⁸.

⁸H. H. Hageman, op. cit., pp. 5-13.

The following pages will contain a discussion of the commercial methods of cracking heavy oils and the systems which were employed to present evidence of the extent of pyrolyzation in the oil under investigation. This will be terminated by an interpretation of the experimentation and research.

CHAPTER II

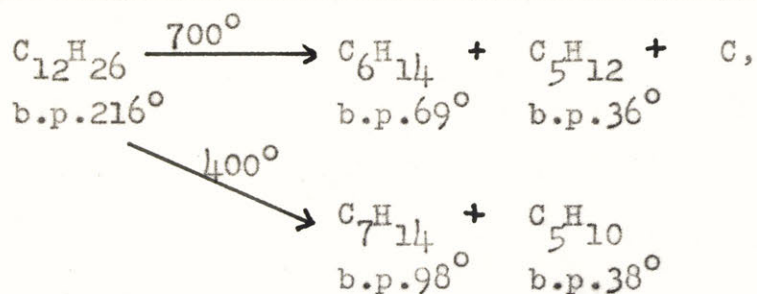
CRACKING AND THE CRACKING PROCESS

A. The Cracking Process

1. The Commercial Cracking Process:

The decomposition of certain products of distillation by subjection to a degree of heat so far above their boiling points that they divide into component parts whose boiling points are lower than the original constituents is known as the cracking process. Cracking may be accomplished in an ordinary fire-still by considering vapors arising from the boiling oil upon the cool dome of the still, whence they drop into the super-heated oil below where they are broken into lighter oils and instantly vaporized, passing over into the condenser. The hypothetical equation written below may be taken as a representative of the types of changes which probably occur¹.

¹J. B. Conant, The Chemistry of Organic Compounds, p. 53.



The Encyclopedia Americana² describes the Barton and

²The Encyclopedia Americana, Volume VIII, p. 147.

the Rittman processes as follows:

a. Barton Process:

Cracking is accomplished in this process by subjecting the entire still system and its distillation products to pressures ranging from 60 to 75 pounds per square inch.

b. Rittman Process:

In this process the vapors from the still are forced through a tube heated to 850° F. with pressures up to 500 pounds per square inch to pyrolyze the oil. The products are then redistilled by vacuum distillation. The yield of lower boiling fractions is from 60 to 70% of the original oil.

2. Description of the Cracking Still

Used in This Investigation

The apparatus used for the attempted cracking of the crude cedar wood oil was the metallic still, described by Hageman³, which operated at atmospheric pressure.

³H. H. Hageman, op. cit., p. 4-5.

Another type of still was employed in an attempt to

crack the oil in a vapor stage. A $3/8$ inch copper tube was attached to a one-liter round-bottom side-arm flask by means of rubber fittings, and the tube was passed over a $2\frac{1}{4}$ -inch series of 12 gas burners. Around the part of the tubing serving as a condenser were placed two water-jackets, through which was forced cooled water to aid in the condensation of the vapors. The liquid and any vapors were to be collected by a series of connected flasks in an ice-bath.

B. Procedure for Cracking

The fraction of oil used in this investigation was obtained in the procedure presented by Hageman⁴.

⁴H. H. Hageman, op. cit., pp. 5-8.

A sample of oil containing fractions boiling from 253.5° to 254.9° C. was placed in the still described above. Heat was applied from a Fisher burner to the one-liter flask and to the condenser tube by a $2\frac{1}{4}$ -inch series of gas burners.

The distillation began immediately upon boiling and continued until all but a few milliliters had been distilled. The writer assumed that the distillation resulted in no appreciable cracking because of the continuous distillation and the lack of visible evidence or odor change.

The above still was reassembled and filled with cedar

wood tar and distilled as previously described. There was apparent evidence of appreciable cracking in obtaining a gas and an oil of less viscosity as the end products from the original tar. This distillate may be used in future investigations to compare the products with those obtained by Shepard⁵.

⁵J. C. Shepard, op. cit., pp. 11-12.

C. Vacuum Distillation of Oil Subjected
to the Cracking Process

The oil was fractionated under reduced pressure as in the method described by Lemmons⁶. The distillate from the

⁶C. A. Lemmons, A Partial Separation of the Constituents of Heart Wood Cedar Oil, Unpublished Master's Thesis, (1936), pp. 17-19.

cracking still was divided into two portions for convenience in handling. The data on the first portion, consisting of 600 ml. of oil, were tabulated in Table I. The second portion, consisting of 650 ml. of oil, was distilled in a like manner, and the data were tabulated in Table II.

The fractions of oil from the vacuum distillation were combined according to refractive indices to effect a more complete separation of the similar products. Fractions 3

through 8 with refractive indices of 1.5003 to 1.5017, as shown in Table I, were combined with numerically identical fractions of oil with refractive indices of 1.5006 to 1.5015, as shown in Table II. The 600 ml. of combined oil was distilled under reduced pressure and the data were compiled in Table III. The remainder of the oil was combined and fractionated, in like manner as the above, with the data recorded in Table IV.

D. Discussion of Data Tables

The 1250 ml. of oil used in obtaining the data in Tables I and II was the yield from 1750 ml. of crude cedar wood oil subjected to the cracking process.

It was interesting to the writer to note that the yield of products boiling at 264° C. or below was approximately 70% of the original oil. The results compare closely with Table II of Lemmons⁷ noting a 70-71% yield of similar products from

⁷C. A. Lemmons, op. cit., p. 11.

crude cedar wood oil.

Fractions 3 through 8 of Table I, with refractive indices of 1.5008 to 1.5017, were combined with corresponding fractions from Table II with refractive indices of 1.5006 to 1.5015. This was attempted for a possible closer grouping

TABLE I

First Vacuum Distillation of Crude Cedar Wood Oil
 Subjected to the Cracking Process

Total Volume: 600 ml. Still Pressure: 2 mm.

Boiling Point Correction = $7 \times .043 = 0.301^{\circ} \text{C.}$ (753 mm.)

Cut #	Pot. Temp. ($^{\circ}\text{C.}$)	Still Head ($^{\circ}\text{C.}$)	Corr. Atm. B.P.	$n_{\text{d}}^{20^{\circ}\text{C.}}$	Volume (ml.)
1	158-178	51-59	231.3	1.4970	50
2	178-179	91-98	242.3	1.5003	50
3	179-180	98-109	248.3	1.5008	50
4	180-180	109-100	248.3	1.5008	50
5	180-180	100-100	248.3	1.5011	50
6	180-179	100-100	249.3	1.5011	50
7	179-179	100-100	250.3	1.5011	50
8	179-179	100-100	250.3	1.5017	50
9	179-178	100-98	250.3	1.5020	50
10	178-182	98-100	251.3	1.5034	50
11	182-192	100-110	256.3	1.5072	50
12	192-	110-	260.3	1.5124	50

TABLE II

First Vacuum Distillation of Crude Cedar Wood Oil

Subjected to the Cracking Process

Total Volume: 650 ml.

Still Pressure: 2 mm.

Boiling Point Correction = $9.5 \times 0.43 = 0.4085^\circ \text{C. (750.5 mm.)}$

Cut #	Pot. Temp. ($^\circ\text{C.}$)	Still Head ($^\circ\text{C.}$)	Corr. Atm. B.P.	$N_d^{20^\circ\text{C.}}$	Volume (ml.)
1	155-173	45-90	198.4	1.4930	50
2	173-175	90-90	246.4	1.5001	50
3	175-176	90-91	251.4	1.5006	50
4	176-176	91-91	251.4	1.5006	50
5	176-177	91-93	251.4	1.5010	50
6	177-173	93-92	251.4	1.5010	50
7	173-173	92-92	251.4	1.5010	50
8	173-175	92-89	251.9	1.5015	50
9	175-175	89-91	253.4	1.5020	50
10	175-177	91-93	251.4	1.5031	50
11	177-179	93-93	251.4	1.5055	50
12	179-196	93-104	256.4	1.5108	50
13	196-205	104-115	264.4	1.5130	30

TABLE III

First Vacuum Distillation of Crude Cedar Wood Oil

Combined by Refractive Indices

Table I, Fractions 3 through 8 - $n_d^{20^\circ\text{C.}}$ of 1.5003 to 1.5017
 Table II, Fractions 3 through 8 - $n_d^{20^\circ\text{C.}}$ of 1.5006 to 1.5015

Total Volume: 600 ml.

Boiling Point Correction = $9 \times .043 = 0.387^\circ \text{C.}$ (751 mm.)

Cut #	Pot. Temp. ($^\circ\text{C.}$)	Still Head ($^\circ\text{C.}$)	Corr. Atm. B.P.	$n_d^{20^\circ\text{C.}}$	Volume (ml.)
1	165-170	77-77	248.4	1.4995	50
2	170-170	77-77	249.4	1.4999	50
3	170-170	77-77	249.4	1.4999	50
4	170-170	77-76	249.4	1.5001	50
5	170-170	76-76	250.4	1.5002	50
6	170-170	76-76	250.4	1.5002	50
7	170-170	76-76	250.4	1.5004	50
8	170-170	76-76	250.4	1.5005	50
9	170-170	76-76	254.4	1.5010	50
10	170-170	76-76	255.4	1.5017	50
11	170-170	76-77	256.4	1.5037	50
12	170-170	77-84	264.4	1.5105	20

TABLE IV

First Vacuum Distillation of Crude Cedar Wood Oil

Combined by Refractive Indices

Table I Fractions 1, 2, 9-12 - $N_d^{20^\circ\text{C.}}$ of 1.4970 to 1.5003
 1.5020 to 1.5124
 Table II Fractions 1, 2, 9-12 - $N_d^{20^\circ\text{C.}}$ of 1.4930 to 1.5001
 1.5020 to 1.5130

Total Volume: 600 ml.

Boiling Point Correction = $11 \times .043 = 0.473^\circ\text{C.}$ (749 mm.)

Cut #	Pot. Temp. ($^\circ\text{C.}$)	Still Head ($^\circ\text{C.}$)	Corr. Atm. B.P.	$N_d^{20^\circ\text{C.}}$	Volume (ml.)
1	148-165	50-72	239.5	1.4959	50
2	165-169	72-74	250.2	1.5003	50
3	169-170	74-76	250.5	1.5009	50
4	170-171	76-76	251.5	1.5013	50
5	171-171	76-77	252.5	1.5015	50
6	171-171	77-77	253.5	1.5020	50
7	171-171	77-77	256.5	1.5028	50
8	171-171	77-78	254.5	1.5039	50
9	171-171	78-80	259.5	1.5059	50
10	171-172	80-85	261.5	1.5092	50
11	172-173	85-95	263.5	1.5134	50
12	173-175	95-98	264.5	1.5141	10

of refractive indices in the sample desired for further investigation (Table III). The light and heavy cuts of Tables I and II were combined and fractionated for possible recombining into the desired fractions (Table IV). This, in part, explains the closer grouping of refractive indices and boiling points shown in Table III and the wider range in Table IV. The lack of a trace of cedrol in any sample may not indicate cracking but only incomplete refractionation in the cracking process.

In the following chapter an attempt will be made to establish whether or not any appreciable amount of cracking occurred.

CHAPTER III

PHYSICAL CONSTANTS AND CHEMICAL REACTIONS

A. Physical Constants

Several of the physical constants were determined. An attempt will be made to compare these constants with some of those found on other samples of oil boiling at approximately 250° C.

In Table V the writer has compared the physical constants of the fraction of oil used in this investigation with those of straight vacuum distilled cedar wood oil and with those of oil that is known to have been pyrolyzed. The fractions used were selected on the basis of their close atmospheric boiling points.

B. Solubility Grouping

1. Qualitative Analysis for Nitrogen, Sulfur and the Halogens:

A sodium fusion with the oil was performed as described by McElvain¹ with the tests for nitrogen, sulfur and the

¹S. M. McElvain, op. cit., pp. 40-41.

halogens giving negative results.

TABLE V

Comparison of Physical Constants with Other Oil Samples

Sample	Atm. B.P.	$n_d^{20^\circ}$	Sp. Gr. $\frac{20}{20}$	Sp. Rot. $\frac{25}{25}$
Cracked oil ²	250.8°	1.5082	.94088	+ 27.9
Oil of this investigation	250.2°	1.5003	.9276	- 37.2
Straight run sample ³	250.0°	1.5011	.9297	

²J. N. Phillips, op. cit., p. 8.

³C. A. Lemmons, op. cit., p. 13.

2. Grouping by Solubility:

In accordance with the procedure found in McElvain⁴ the

⁴S. M. McElvain, op. cit., p. 74.

solubility grouping was determined. The data are recorded in Table VI.

According to the reaction of the sample towards the various solvents, the oil is a member of McElvain's Group V. This group may contain any or all of the following:

- a. unsaturated hydrocarbons
- b. some highly alkylated aromatic hydrocarbons

TABLE VI

Solubility of Cut #2, Table IV

Reaction Toward	25° C.	100° C.
Water	insoluble	insoluble
Ether	soluble	soluble
NaOH (5%)	insoluble	insoluble*
HCl (5%)	insoluble	insoluble
H_2SO_4	partially soluble	partially soluble**
H_3PO_4 (5%)	insoluble	insoluble
Ethyl Alcohol (95%)	partially soluble	infinitely soluble
Chloroform	soluble	soluble
Acetone	soluble	soluble
Carbon Disulfide	soluble	soluble
Carbon Tetrachloride	soluble	soluble

* Formed an emulsion with the oil.

** Change in viscosity accompanied by evolution of heat. The oil layer turned brown and the acid black upon standing.

- c. aldehydes
- d. ketones
- e. esters
- f. anhydrides
- g. alcohols
- h. ethers and acetals
- i. acyl halides and other halogen derivatives of classes c, d, e, f, g, and h.

C. Class Reactions

1. Tests for Unsaturation:

a. Bromine in Carbon Tetrachloride: Approximately 0.2 ml. of the oil was dissolved in 2 ml. of carbon tetrachloride and treated dropwise with 5% solution of bromine in carbon tetrachloride until the bromine color persisted. The decolorization of the bromine solution suggested that the oil contained considerable amounts of unsaturates.

b. Dilute Aqueous Potassium Permanganate: A 0.2-ml. portion of the oil was put in solution with 2 ml. of acetone and treated dropwise with a 2% aqueous solution of potassium permanganate until a purple color persisted. The results confirmed the conclusion drawn from the bromine solution test.

2. Reaction of Aldehydes and Ketones:

a. 2,4-Dinitrophenylhydrazine: A 2-ml. sample of the oil under investigation was placed in 3 ml. of the 2,4-dinitrophenylhydrazine reagent, and the mixture was allowed to stand at room temperature. The formation of a yellow precipitate was taken as a positive test for an aldehyde or a ketone.

b. Tollens' Solution: To 2 ml. of Tollens' solution in a test tube, cleaned with nitric acid, were added 2 drops of the oil, and the mixture was warmed in a beaker of hot water. A silver mirror was formed on the tube, thus confirming the presence of an aldehyde.

3. Neutral Equivalent:

An accurately weighed sample of oil was dissolved in approximately 50 ml. of alcohol and titrated against a standardized 0.1N solution of sodium hydroxide to the phenolphthalein end point. The neutral equivalent was calculated to be 792. The conclusion was drawn that one or more acids was present in relatively small amounts.

4. Reaction with Sodium:

Two small, thin slices of freshly cut sodium were added to a 0.5-ml. portion of the oil. A vigorous reaction immediately followed liberating hydrogen gas, and a brown formation appeared on the sodium. This reaction does not necessarily constitute a test for an alcohol since acids, and some aldehydes and ketones, react with sodium to liberate hydrogen.

D. Separation of a Water-Insoluble Mixture

Following the procedure described in McElvain⁵, an at-

⁵S. M. McElvain, op. cit., pp. 161-162.

tempt was made to separate the constituents of the oil under

investigation. Apparently there was a trace of acid(s) present in the oil although the bulk separated as neutral components, thus corresponding to the solubility grouping previously presented.

E. Oxidation of the 250.2° C. Reaction

Three oxidations with concentrated nitric acid were performed on the oil sample by the procedure outlined by Lemmons⁶, of which the following is representative.

⁶C. A. Lemmons, op. cit., p. 35.

A 10-ml. portion of the oil was placed in a round-bottomed flask which was attached to a reflux condenser, and the contents were heated over a water-bath. Concentrated nitric acid was added dropwise until the reaction appeared to be complete. The mixture was allowed to cool to room temperature and was made basic with dilute ammonium hydroxide. The solution was filtered, and the precipitate was retained for further investigation. The filtrate was made acidic with 1:8 hydrochloric acid, and the precipitate was collected on a Buchner funnel.

Recrystallization of the acidic precipitate was attempted from alcohol, alcohol-water mixtures, diethyl ether, acetone, petroleum ether, and diethyl ether-petroleum ether mixtures

with no success. In each case the precipitate was recovered in the form of a red-brown gum with no crystals present.

The precipitate formed on the addition of ammonium hydroxide was found to be soluble in an excess of the reagent when heated to boiling. Attempts to recrystallize the substance from the common solvents met with failure.

CHAPTER IV

SUMMARY

Two methods to attempt the cracking of crude New Braunsfels cedar wood oil have been presented. The stills used for these methods have been described. The data concerning the fractionation of the oil, subjected to the cracking processes, have been presented.

Evidence has been presented, through comparison of physical constants, indicating that there was no appreciable extent of cracking in the oil used throughout this investigation.

Some chemical reactions of the oil have been given. The writer found that this fraction of oil contains unsaturates, an appreciable amount of aldehydes and ketones and relatively small amounts of acid.

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