CRUDE OIL ANALYSIS

By DAVID WESSON

The discussions at the 1926 meeting of the American Oil Chemists Society have shown that the time is now ripe to discard the refining test, so long used in determining the value of crude vegetable oils, and resort to scientific methods of chemical analysis.

There was a time when iron masters bought iron ore for their furnaces on what was known as the crucible assay. A known weight of ore, limestone and powdered charcoal or coke were heated in a Hessian crucible in a coke fire for several hours, after which the crucible was withdrawn, cooled, and broken, and a button of iron, separated from the slag and weighed. This was taken as the amount of iron present in the ore. Like our refining test it was uncertain in results, depending a good deal on the skill of the operator and the character of the ore. At the best, it was a rough test, and perhaps good enough for the primitive plants of its day.

With the advent of the chemist in the iron industry, it was found possible to determine exactly how much iron was contained in an ore, and the character of impurities which would influence the yield in the furnace, and the quality of the product. This information put a correct value on the ore. There is no logical reason why such methods should not apply to the valuation of crude cottonseed oil.

In 1916 and 1917, the writer, working on the problem of improving refining methods, concluded that the first step was to find out how to analyze the oil so as to have some basis for getting at the efficiency of refining operations and the causes which influenced the losses.

With the assistance of Harold P. Gaylord, a method was worked out in the writer's laboratory. It was tested in other laboratories, and several years after was carefully checked up by Dr. Geo. P. Jamieson, of the U. S. Bureau of Chemistry. The method shows, absolutely, the amount of refined oil present in a given sample of crude oil, and gives a standard by which a refining operation or method can be judged.

In applying it to commercial practice, allowance would naturally have to be made for the efficiency of refining operations in the plant, in getting at the value of the oil to the purchaser. If the refiner does not work to a high state of efficiency, that is his own misfortune; not the fault of the man who sells the crude oil. If the man who sells the crude oil, pumps water and settlings into it, the result will be apparent in the sample when analyzed.

The following description of the test is given as written in 1917, and the numerous examples of its application bear tribute to its accuracy:

Absolute Method for Oil Analysis

The object of this method is to determine the maximum amount of refined oil which can be produced from a given sample of crude or partly refined oil and at the same time to determine the amount of fat necessary to saponify and the amount of caustic soda necessarily absorbed in the refining of the oil.

It has been found as the result of careful experiment that when an oil is dissolved in gasoline the mixture of oil and gasoline can be shaken up with a large excess of caustic potash, which will combine with the coloring matter, free fatty acids, and break up the lipoid bodies in the cold inside of 3 minutes. By adding a considerable quantity of 50 per cent alcohol and water the excess caustic, together with the soap and products of decomposition of the organic matter, color, etc., settles out, leaving a clean gasoline solution of refined oil which can be readily separated from the solution of soap-stock.

After washing all oil out of the alcohol solution of soap-stock there is no difficulty in running the latter down to dryness and determining the fatty acids therein by following the regular procedure. It is also possible by this method, operating on a separate weight of oil, to determine the alkali absorbed, which is done by titrating a blank representing the caustic potash started with and titrating the excess alkali in the alcohol soap solution, using phenolphthalein as an indicator.

APPARATUS:

A quantity of 4-ounce oil sample bottles.

A wash bottle blow-off arrangement such as is used for soap-stock tests.

Soxhlet flasks.

Erlenmeyer flasks.

A pipette graduated to deliver 10 grams of oil at 20° C.

Acid and alkali burettes.

REAGENTS:

Redistilled gasoline, less than 80° B. P. Cent.

Fifty per cent grain alcohol. (Denatured will not do.)

Caustic potash, 14 per cent solution. (Caustic soda will not do.)

Phenolphthalein.

Quarter or half normal HCl.

Quarter or half normal NaOH.

PROCESS: Pipette 10 grams of a well shaken sample into a small tared beaker and then take the exact weight of the oil. Wash the oil into a 4-ounce sample bottle, using 50 cc. of gasoline for the purpose. Pipette 10 cc. KOH solution into the well mixed oil and gasoline and shake for 3 minutes. Then measure in 25 cc. 1 to 1 alcohol and shake vigorously until the soap separates easily. In some oils the separation is almost instantaneous: in other oils it is very slow. As soon as a good separation is shown, which should be in less than a minute, whirl in centrifuge and let stand a few minutes before blowing off the gasoline solution of the oil into a clean tared Soxhlet flask. Shake up twice, using 20 cc. of gasoline each time. Blow off the same after each washing into Soxhlet flask. Time can be saved by whirling after each addition of the gasoline. Distill off the

---

Table No. 1.—Showing Possible Accuracy of Absolute Oil Test

	Absolute Oil	
Samples	A	B
Sav. 39-a	96.79	96.82
" 35-b	97.05	97.10
" 43	97.	96.80
" 44	96.95	96.97
" 34	96.03	96.20
" 40-b	96.73	96.65
" 37-e	94.05	94.
" 41-d	96.83	96.95
" 36-a	96.79	96.85
" 38-c	97.19	97.32
B 312	97.05	97.07
" 310	95.79	95.55
" 309	97.20	97.32
" 317	97.73	97.63
Sav. Comp. No. 1	96.97	96.90
N. O. " " 1	96.75	96.57
Sav. " " 2	96.65	96.60
Memphis No. 2	97.33	97.30

	Absolute Oil	
	A	B
N. O. No. 2	96.95	97.15
Mem. 54-A	96.57	96.57
Check No. 1	96.75	96.65
" " 2	96.90	96.87
" " 2 (Centrifugal)	97.17	97.27
B. Comp. No. 5	97.23	97.39

Table No. 2.—Results Obtained by Applying the Absolute Test to Refined Oils

Oil	Absolute Oil	Absolute Loss	Moisture	F. F. A.	
B. 312	99.80	.20	.16	.06	.22
B. 309	99.78	.22	.14	.05	.19
B. 311	99.83	.17	.18	.07	.25
B. 317	99.79	.21	.16	.04	.20
B. 310	99.75	.25	.18	.03	.21
N. O. 110	99.80	.20	Present but not determined		
Deodorized* Oil	99.84	.16	" " " "		

Table No. 3.—Method of Reporting Results

No. Refinings	Memphis No. 8	Bayonne No. 11	N. O. No. 7	Sav. No. 8
Date	3/17/17	3/12/17	3/3-3/9/17	No Date
Absolute Oil	96.85	97.07	96.25	95.49
Absolute Loss	3.15	2.93	3.75	4.51
F. A. as Soap	1.58	1.55	1.95	2.95
Loss Not Fat	1.57	1.38	1.80	1.56
NaOH Absorbed	.365	.365	.415	.555
NaOH for F. F. A.	.160	.172	.235	.365
F. F. A.	1.13	1.21	1.66	2.58
F. A. as Soap—F. F. A.	.44	.34	.29	.37
Color Drops	Slowly	Slowly	Quickly	Quickly

Table No. 4.—Showing Accuracy of Checks When Determining Absolute Oil

12 Bayonne Refinings

Number	1 Absolute Oil	2 Absolute Oil	Difference
159	98.10	97.90	.20
160	97.45	97.50	.05
161	97.67	97.43	.24
162	97.39	97.56	.17
163	97.70	97.66	.04
167	97.83	97.77	.06
177	97.27	97.20	.07
173	97.50	97.60	.10
175	97.27	97.20	.07
178	96.99	96.93	.06
169	97.73	97.65	.08
168	97.90	97.80	.10
12	Average		.103

8 New Orleans Refinings

Number	1 Absolute Oil	2 Absolute Oil	Difference
92	96.83	96.73	.10
97	97.47	97.47	.00
106	96.60	96.55	.05
110	97.63	97.67	.04
111	97.07	97.07	.00
113	98.40	98.29	.11
124	96.47	96.35	.12
91	96.90	96.97	.07
8	Average		.06

8 Memphis Refinings

Number	1 Absolute Oil	2 Absolute Oil	Difference
76	96.99	96.99	.00
2	98.67	98.67	.00
55	97.23	97.30	.07
1	97.89	97.37	.23
3	98.64	98.84	.20
73	97.00	97.30	.30
75	98.65	98.55	.10
77	97.39	97.43	.04
8	Average		.117

Table No. 5 (a)

Analyses of Bayonne Refinings

Number	Absol. Oil	Absol. Loss	Alk. Abs.	F. S. as S.	Loss not Fat	F. F. A.
159	98.00	2.00	.30	1.10	.90	1.00
160	97.47	2.53	.36	1.51	1.02	1.10
161	97.55	2.45	.28	1.40	1.05	.90
162	97.47	2.53	.30	1.28	1.25	1.00
163	97.68	2.32	.25	1.51	.83	1.00
177	97.23	2.77	.51	1.73	1.04	1.30
173	97.55	2.45	.36			.90
175	97.23	2.44	.40	1.45	1.32	.90
178	96.96	3.04	.45	2.25	.79	1.60
169	97.69	2.31	.38	1.68	.63	1.20
168	97.85	2.15	.30	1.40	.75	1.00

Table No. 5—(Continued)

Application of Analyses

Number	F. F. A.	Absol. Oil	Absol. Loss	Kettle Loss	Kettle Yield	Efficiency
159	1.00	98.00	2.00	4.91	95.09	97.
160	1.10	97.47	2.53	6.21	93.79	96.2
161	.90	97.55	2.45	6.66	93.34	96.
162	1.00	97.47	2.53	6.62	93.38	95.8
163	1.00	97.68	2.32	6.20	93.80	95.
177	1.30	97.23	2.77	6.32	93.68	97.
173	.90	97.55	2.45	4.93	95.07	97.4
175	.90	97.23	2.77	6.01	93.99	97.
178	1.60	96.96	3.04	7.09	92.91	95.8
169	1.20	97.69	2.31	6.64	93.36	95.6
168	1.00	97.85	2.15	4.35	95.65	97.8
Average	1.08	97.52	2.48	5.99	94.01	96.51

Table No. 5 (b)

Analyses of Memphis Refinings

Number	Absol. Oil	Absol. Loss	NaOH	F. A. as Soap	Loss not Fat	F. F. A.
76	96.99	3.01	.34	1.35	1.66	.7
2	98.67	1.33	.24	1.11	.22	.9
55	97.26	2.74	.29	1.62	1.12	1.00
1	98.00	2.00	.25	.79	1.21	1.00
3	98.74	1.26	.20	.84	.42	.8
73	97.15	2.85	.34	1.58	1.27	1.2
75	98.60	1.40	.21	.85	.55	.8
77	97.41	2.59	.34	.77	1.82	.9

Application of Analyses

Number	F. F. A.	Absol. Oil	Absol. Loss	Kettle Loss	Kettle Yield	Efficiency
76	.7	96.99	3.01	6.72	94.28	92.20
2	.9	98.67	1.33	5.54	94.46	95.76
55	1.00	97.26	2.74	5.00	95.	97.70
1	1.00	98.	2.00	6.05	93.95	95.90
3	.8	98.74	1.26	4.91	95.09	96.22
73	1.2	97.15	2.85	6.57	93.43	96.17
75	.8	98.60	1.40	4.89	95.11	96.46
77	.9	97.41	2.59	5.86	94.14	96.64
Avg.	.91	97.85	2.15	5.69	94.42	96.38

Analyses and Application of 12 Savannah Refinings

Table No. 5 (c)

No.	F.F.A.	Kettle Loss	Kettle Yield	Absolute Oil	Absolute Loss	Alkali Absorp.	NaOH for F.F.A.	F.F.A.	Efficiency
39a	1.7	8.26	91.74	96.80	3.20	.49	.23	1.64	94.80
35a	1.55	6.78	93.22	97.08	2.92	.40	.22	1.55	97.02
43	.95	6.54	93.46	96.90	3.10	.34	.16	1.13	96.46
44	1.35	7.28	92.72	96.96	3.04	.42	.19	1.34	95.62
42e	1.35	7.83	92.17	98.02	1.98	.31	.18	1.27	94.06*
45b	1.00	7.68	92.32	96.68	3.32	.41	.12	.84	95.50
34b	2.65	7.56	92.44	96.11	3.89	.55	.36	2.54	95.70
40b	1.10	7.70	92.30	96.69	3.31	.47	.16	1.09	95.46
37e	3.60	8.18	91.82	94.00	6.00	.81	.51	3.60	97.68**
41a	.95	7.34	92.66	96.89	3.11	.52	.18	1.23	95.64
36a	1.25	6.42	93.58	96.82	3.18	.49	.16	1.13	96.68
38c	1.15	7.02	92.98	97.25	2.75	.46	.15	1.06	95.62
Avg.	1.55	7.38	92.62	96.68	3.32	.45	.22	1.54	95.85

*Peanut Oil.
**Cold Pressed—Also Off.

Table No. 5 (d)

	Bayonne	New Orleans	Memphis
No. Refinings	11	9	8
Average F. F. A.	1.08	1.53	.91
" Loss by Oil	5.99	6.31	5.69
" Absolute Loss	2.48	2.95	2.15
" Loss not Fat	.96	.99	1.03
" F. A. as Soap	1.53	1.86	1.11
" Kettle Yield	94.01	93.68	94.31
" Absolute Oil	97.52	97.15	97.85
" Efficiency	96.51	96.48	96.38
NaOH Absorbes	.39	.35	.28

Effect of Settling Crude Oil

Table No. 6

	1	73	76
ABSOLUTE OIL:			
Whole Sample	98.	97.15	96.99
Settled Sample	99.5	98.60	98.82
Difference	1.5	1.45	1.83
ALKALI ABSORPTION:			
Whole Sample	.25	.34	.34
Settled Sample	.18	.25	.16
Difference	.07	.09	.18
F. A. AS SOAP:			
Whole Sample	.79	1.58	1.35
Settled Sample	.60	1.32	.71
Difference	.19	.26	.64
LOSS NOT FAT:			
Whole Sample	1.21	1.27	1.66
Settled Sample	.15	.08	.47
Difference	1.06	1.19	1.19
FREE FATTY ACID:			
Whole Sample	1.00	1.20	.70
Settled Sample	.64	1.13	.64
Difference	.36	.07	.06
NaOH (Acidity No.)			
Whole Sample	.14	.168	.098
Settled Sample	.09	.16	.090
Difference	.05	.008	.008

Analysis of Cold Pressed Oil from New Orleans

Table No. 7

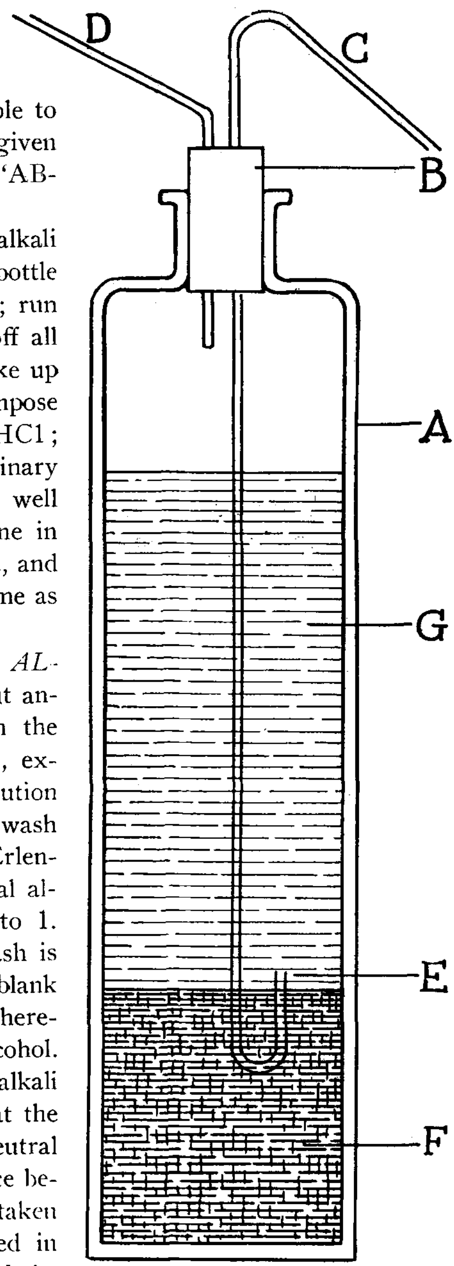
Absolute Oil	97.32
Absolute Loss	2.68
Alkali Absorption	.67
F. A. as Soap	1.05
Loss Not Fat	1.63
F. F. A.	1.48
P_2O_5	.049

Alkali absorption may not be O.K. Alcohol solution was nearly black and end point was very uncertain.

gasoline; warm over lamp till gasoline vapors are all driven off; cool and weigh. The result will be the amount of actual refined oil possible to obtain by alkali refining from a given sample of crude. This is called "ABSOLUTE OIL."

F. A. AS SOAP: Wash the alkali solution remaining in 4-ounce bottle into a beaker or evaporating dish; run down on the steam bath to drive off all alcohol and gasoline remaining; take up in 150 to 200 cc. of water; decompose with excess of dilute H_2SO_4 or HC1; collect the fatty acids as in ordinary analysis of soap-stock; wash them well on filter; extract with cold gasoline in a tared flask; drive off the gasoline, and weigh the fatty acids, reporting same as "FATTY ACIDS AS SOAP."

DETERMINATION OF ALKALI ABSORBED: Measure out another portion of the oil; treat in the same manner as for Absolute Oil, except the two washings of soap solution with 20 cc. gasoline are omitted: wash from the 4-ounce bottle into an Erlenmeyer flask, using 30 cc. of neutral alcohol, which must be at least 1 to 1. At the same time the caustic potash is added to the oil run 10 cc. for a blank into an Erlenmeyer flask and add thereto 25 cc. of the same 1 to 1 alcohol. When the titration of the excess alkali is made in the soap solution add at the same time 30 cc. of the same neutral alcohol to the blank. The difference between the quarter normal HC1 taken up by the blank and that required in the soap solution is the measure of the amount of alkali absorbed by the oil. This determination should be made quickly, as the results are apt to be too



Sketch of Wash Bottle Arrangement for Making the Analysis Under Discussion.

A 4 oz. sample bottle; B cork with two perforations; C blow-off tubes with broken end at E; D blow tube; F alcohol potash soap layer; G gasoline oil layer.

high if the solutions are allowed to stand around any length of time. By titrating in an Erlenmeyer flask over a piece of white paper or a white dinner plate it is not difficult to get the end point with phenolphthalein.

Accuracy of Method

The method has been tried out thoroughly during the last two months.*

Table No. 1 shows check results on Absolute Oil on crudes taken from a variety of sources. Plenty more of similar checks can be furnished.

Table No. 2 shows the results of applying the method to refined oils. Samples marked "B" were from different refinings at Bayonne. It will be noted in looking at this table that the sum of the F. F. A. and the moisture is a remarkably close check on the Absolute Loss as shown by the method. Results given on New Orleans No. 110 and 88 oil were made before it occurred to us to find out the reason for the Absolute Loss. The 88 oil in question came from Bayonne at a time when the plant was not running properly and unquestionably contained moisture and some F. F. A., probably about .03 to .04 per cent. The New Orleans sample was taken from the refining kettle and doubtless would, if tested for moisture and F. F. A., show up about the same as the Bayonne samples.

Reporting of Results

Table No. 3 gives analyses of composite samples sent from different refineries. It also shows the way the results should be reported. The Loss Not Fat as shown on this report is the difference between the F. A. as Soap and the Absolute Loss. In order to determine the organic matter in the Loss Not Fat, the crude should be analyzed for moisture and the percentage of moisture subtracted. The NaOH absorbed shows the amount of caustic necessary theoretically to refine the oil. Below this is shown the NaOH necessary to combine with the F. F. A. The difference between these two factors shows the actual excess of NaOH necessary to combine with the organic matter and form the F. A. found as soap, which latter comes from the breaking down of complex glycerider. The F. F. A. is determined very carefully in the usual manner. The F. A. —F. F. A. shows the amount of fatty acids saponified over and above the free fatty acid, and it is necessary to saponify this much free fatty acid before the oil can be refined. This has been determined by careful experiment. The last line shows whether the color drops slowly or quickly after shaking up with alcohol in the Absolute Oil Test. We have found that when the color drops slowly an oily soap-stock or high Free Oil Loss almost invariably happens.

Further tests showing accuracy of results, are shown in Table No. 4.

* i.e., from March 22, 1917.

which gives checks on (12) Bayonne refinings, (8) New Orleans, and (8) Memphis refinings.

The application of analyses to actual refinings are shown in Table No. 5, which gives analyses and their application to refinings from different plants.

It is interesting to note, that with the prime crude worked, the average kettle efficiency was very close to 96.5 per cent. The tables show also that absolute oil and kettle efficiency are not entirely governed by free fatty acid.

Effect of settling of crude oil is shown very fully in Table No. 6, where the absolute oil is greatly increased by the settling of the crude oil samples, taken from different refinings.

Thorough settling on the three samples tested, showed 1.45 to 1.83 per cent difference between the whole sample and the well settled one. This is mostly due to the loss, not fat in the oil.

The analysis of cold pressed oil, given in Table No. 7, is interesting as showing an apparent F. F. A. of 1.48 per cent, whereas only 1.05 fatty acid would accur as soap. In other words, the gossypol titrating as F. F. A. gives an erroneous result, and free fatty acids determined in the usual way are frequently not free fatty acids at all.

Summary

It has been shown that it is easily possible to obtain the exact amount of refined oil in a given sample of crude by an accurate analytical method.

The refining efficiency in a well operated refinery is 96.5 per cent on prime crude oils.

That proper settling of crude oil results in an increase of the absolute oil of 1.5 per cent and upwards.

That the free fatty acid test may show acidity due to other causes than free fatty acids.