• *Tall Oil Symposium* [1]

Tall Oil—A Growing Source of Fatty Acid and Rosin

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The American Oil Chemists' Society has had an active part in several phenomenal developments of vegetable oils. Brought into being by a handful of chemists interested in cottonseed oil, it has during its relatively short existence contributed to the changing of cottonseed oil by refining, hydrogenation, and deodorization from a dark, reddish, bad-smelling, inedible oil to a major source of salad oil, margarine, and shortening.

Then came soybeans, practically unheard of in this country until the late '20's but now grown in such magnitude that its oil crop is almost double that of cottonseed. Not only is more soybean oil used for edible purposes than cottonseed oil, but much of it has gone into the paint and resin field where, because of its semi-drying qualities, it competes with linseed, tung, fish, and other drying oils.

From the cotton of the South to the soybeans of the Middle West, we again return to the South; and at this spring meeting in the Cotton Capital we pay homage to a new and healthy member of the vegetable oil tribe, tall oil.

Now tall oil, although it is quite different from cottonseed or soybean oil in that it is not a glyceride and contains a high percentage of rosin acids as well as fatty acid, is truly of vegetable origin and does, by virtue of its increased production and expanding use, deserve the recognition the A.O.C.S. is giving it. The symposium will cover the physical and chemical properties of tall oil, recovery and refining methods, analytical methods as well as many of its uses. The purpose of this paper is briefly to review the growth of tall oil and illustrate by a few charts the position it now occupies in the fatty acid and naval stores industries.

When the sulphate process for converting wood to paper pulp was originated in 1884, there was little thought given to the recovery of the fat that existed in the wood pulp. The black tarry soap made when wood chips are autoclaved with strong alkalis was originally washed from the pulp and discarded. Then chemists realized that this material could be burned and the inorganic salts recovered and re-used for digesting the pulp. Later it was determined that the fatty acid and rosin contained in the semi-solid sticky material might be separated from the lignin, acidulated, and put to industrial uses. How well they have succeeded in making this material a valuable industrial product is well shown in the following figures.

In 1940 about 30,000,000 lbs. of crude tall oil were recovered as the acidulated soap, and last year some 600 to 700 million lbs. of crude tall oil were produced. Inspection of the chart shows tall oil's rapid growth and its comparative position in regard to soybean, cottonseed, and linseed oils. While it cannot be directly compared with soybean and cottonseed because they are glycerides and edible, still it is one of the principal sources of vegetable fatty acids for industrial purposes. The tremendous effect that this new material is playing in connection with the fatty acid business is readily noted by comparison with oleic acid.

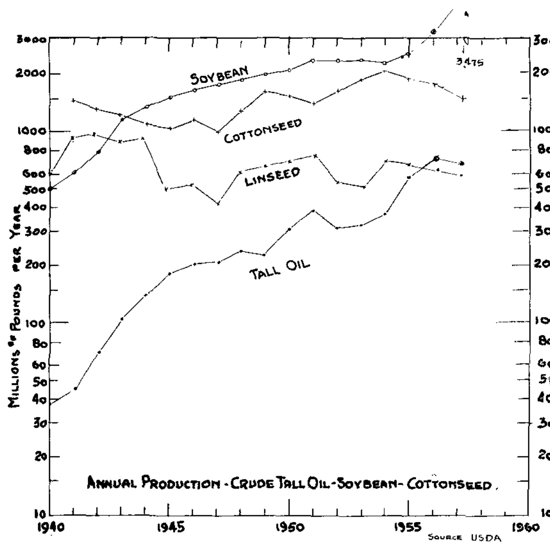

FIG. 1. Production of crude tall oil.

The main commercial unsaturated fatty acid is oleic acid, and its annual production is about 90,000,000 lbs. The production of crude tall oil rose above the production of oleic acid in 1942 and is now more than six times as great as oleic acid, which has remained relatively constant. One must, of course, consider that tall oil is composed of both rosin and fatty acid; consequently only 35 to 50% of the crude tall oil production is fatty acid. Even 35% of the 600,000,000 lbs. however is almost three times the amount of total oleic acid produced.

Fortunately industry has been able to consume at a pace equal to the production of both items up to the present. However this may no longer be possible if the tall oil production continues to grow at its present rate. Regardless of the fatty acid market, we predict the production of tall oil will continue to increase because it is equally as important as a source of rosin as it is of fatty acid.

The production of gum rosin has steadily decreased, possibly because of the increasing cost of harvesting. Modern methods, etc., may correct this to some extent, but the chances are that its production will continue to decline. Wood rosin, on the other hand, has grown very markedly since the '30's and continues to be the major source of rosin. How much longer wood rosin can hold this position is somewhat problematical. Men closely associated with the wood rosin industry say the source of wood rosin, pine stumps, are gradually be-

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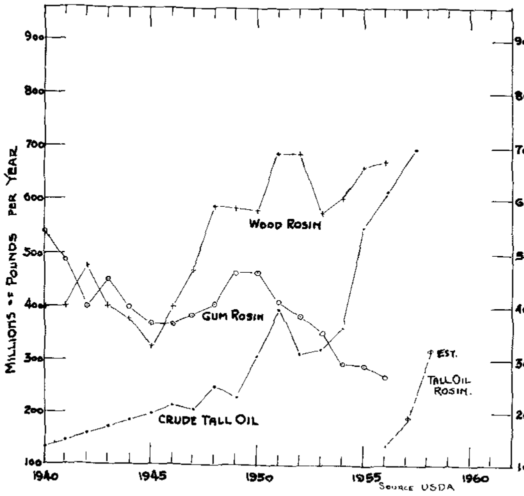

Fig. 2. Rosin production.

ing used up or are in isolated locations and at such distances from present plants that transportation is quite a problem. Also stumps from recent cutting are smaller and contain less rosin than those remaining in the ground from original cutting. With the prospects of diminishing yields of rosin, it is only logical that the rosin people are turning towards tall oil as the new source of rosin.

Early refining processes usually consisted of making an over-all distillation of the crude tall oil, which yielded a distillate containing a mixture of fatty acid and rosin; or the crude tall oil was dissolved in kerosene and treated with H_2SO_4 for improvement in color and odor. Modern refineries now separate the rosin from the fatty acid by fractional distillation, which produces an excellent grade of rosin, pale in color and containing about 2.5% of free fatty acid; a tall oil fatty acid containing less than 1% of rosin acids; a small amount of distilled tall oil containing 35% rosin; a volatile odor fraction containing unsaponifiable material; and a tall oil pitch. The rapid growth of these distillation plants is shown on the next chart.

As shown in Table I, there will be capacity in this country by the end of 1958 to convert more than 600 million lbs. of crude tall oil into fatty acid and rosin. This is about two-thirds of the anticipated crude tall oil production. It is also known that some of these plants are planning additions to their plants, so the trend to separate the fatty acid completely from the rosin is sure to continue and one can readily appreciate the tremendous impact that this development will have on both the fatty acid and the rosin industries.

TABLE I

Tall Oil Fractionation Plants

Company	Location	Capacity Million lbs/yr.	Date on stream
Armour Chemical	Chicago, Ill.	10	1942
Arizona Chemical	Panama City, Fla.	168	1949 and 1955
Heyden-Newport	Bay Minette, Ala.	72	1954
W. Va. Pulp & Paper	Charleston, S. C.	48	1955
Crosby Chemicals	Picayune, Miss.	96	1955
Hercules Powder	Savannah, Ga.	72	1956
Hercules Powder	Franklin, Va.	72	1956
Union Bag-Camp	Savannah, Ga.	48	1956
Glidden	Port St. Joe, Fla.	48	1957
Monsanto-Emery	Nitro, W. Va.	48	Spring 1958
	Total	682	

Estimated Potential	Low rosin fatty acid	210	millions of pounds per yr.
	Tall oil rosin	320	
	Pitch & by-products	150	

Source: C. & E. News, Sept. 9, 1957

While tall oil came into its own during World War II because of a shortage of fats, it never became involved in price fluctuations which occur in connection with oils used for edible products and those oils which yield glycerine. Tall oil fatty acids have not been used as an edible oil to our knowledge. However the best fatty acids now being produced are bland and light in color and, if esterified with glycerol, might well make a good salad oil. Considering the change in our price structure during the post-war years, we believe manufacturers of tall oil showed great foresight in hammering away at new methods to improve tall oil, thus making it available at comparatively low, steady prices. This development certainly has been one of the major factors in the phenomenal growth.

Figure 3 shows the comparatively stable price of tall oil since its introduction around 1940. One will notice that edible oils have taken a big surge in price levels, especially after the controls were taken off after the war. Stable-priced raw materials are extremely important to the manufacturer of chemicals. One of the hazards of making organic chemicals from fats is the fluctuating price of the raw material. Most chemicals enjoy a rather steady price pattern, and if fat chemicals are to be competitive with those from petroleum, natural gas, etc., their price should remain reasonably stable. The price of crude tall oil has been stable and therefore very desirable to manufacturers of fat chemicals and associated products.

Low stable prices alone cannot account for tall oil's rapid growth, and much credit is due to the versatile and novel mixture of the product itself. Commercial acceptance, while slow initially, spread rapidly for whole crude tall oil, acid-refined, and straight-distilled tall oil. The mixture of fatty acid and rosin, in varying percentages and in various grades, enters into the manufacture of so many products that it is almost impossible to obtain reliable data as no one source can possibly collect sufficient information from consuming industries to balance the production figures.

The Tall Oil Division of the Pulp Chemicals Association, 122 E. 42nd street, New York, has been trying for several years to improve the accuracy of

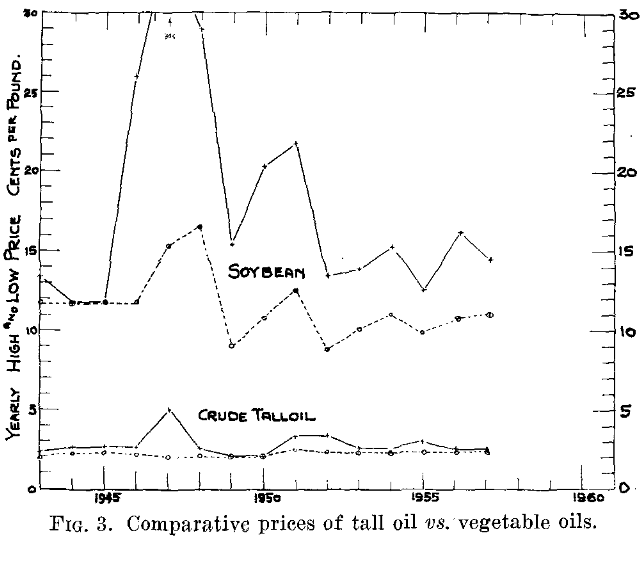

Fig. 3. Comparative prices of tall oil *vs.* vegetable oils.

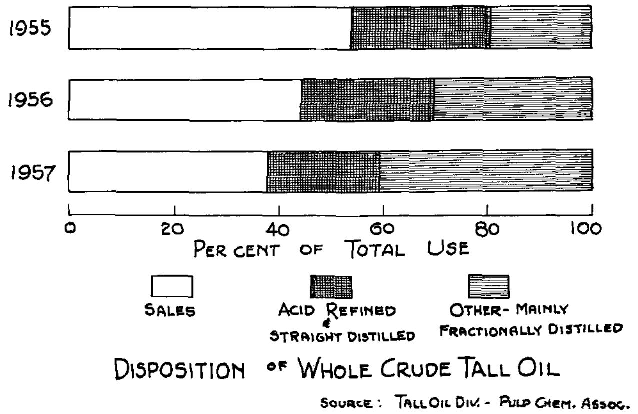

FIG. 4. Disposition of crude tall oil.

this information, and much of the data used in this paper has been obtained from them. While individual uses are many, they can be classified into two main divisions: as a raw material for numerous surfactants, *e.g.,* soaps, asphalt additives, lubricants, flotation chemicals, fat chemicals, etc.; and as a drying oil component in the manufacture of core oils, linoleum, oil cloth, floor tile, driers, paints, varnishes, printing inks, etc.

In some of these uses the mixture of rosin and fatty acids serves as a superior raw material to either one or the other; and it is to be expected that a substantial quantity of the whole oil, either in the crude or its refined form, will continue to be used.

The percentage of the total production of crude oil used as such will undoubtedly diminish, and the future will find increasing amounts being separated into its component parts, *i.e,* low-boiling unsaponifiable, saturated acids, oleic and linoleic acids, solid rosin, sterols, and pitch.

Until 1955 about two-thirds of the refined tall oil sold were acid-refined. In 1955 distilled tall oil increased to half the total, and now we find more than 80% of the refined tall oil is fractionally distilled.

Obviously the future of the tall oil industry is tied up directly with the sulphate pulp industry. The average yield of tall oil varies from mill to mill, both because of the source of the pine and the effectiveness of their recovery methods. It is generally accepted that about 90 lbs. of crude tall oil can be produced with each ton of pulp made. Not all mills achieve this yield, but, in general, good practice will produce this amount from average pine.

Using these figures, we find it would be possible to produce one billion lbs. of tall oil for the year 1958. Estimates for the future show that by 1970 or 1975 we can expect a production of about 1,550,000,000 lbs. of tall oil. The amount of fatty acid that can be produced from this volume is greater than the present fatty acid production from all sources. When one realizes that not only can these acids replace the unsaturated acids of soybean, cottonseed, red oil, and the like but also that they can readily be hydrogenated to stearic acid, it is easily understood that this production will have a great impact on the fatty acid industry. Even by-products, such as the palmitic acid, become a sizeable quantity when we talk of amounts of this nature. Three per cent of 1,550,000,000 lbs. is a sizeable quantity of palmitic acid if it is recovered.

Tall oil is truly a unique and valuable material and is growing in available supplies, in new refineries, in new uses, and new products.

REFERENCES

1. Cannon, Donald R., p. 142, Chem. Engr., June, 1954.
2. "Tall Oil in Industry," Bulletin No. 17, Tall Oil Division of the Pulp Chemicals Association.
3. "Naval Stores Industry Today," Chem. & Engr. News, p. 16, vol. 35, No. 36.

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Production Methods for the Manufacture of Crude Tall Oil and Its Subsequent Processing

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VARIOUS SPECIES of pine trees contain varying amounts of fatty acids and rosin acids. In the kraft pulping operation the pine chips are cooked at a relatively high temperature with a strong alkali. In addition to its primary purpose of dissolving the lignin which holds the cellulose fibers together, this cooking operation also saponifies the fatty acids and the rosin. These soaps in turn are washed out of the pulp along with the dissolved lignin and sent back through the chemical recovery operation. In this the spent or black liquor which contains the dissolved fatty and rosin soaps is passed through multiple-effect evaporators for concentrating the black liquor to a point where it may be burned in special high-pressure boilers for recovery of the inorganic chemicals and the production of steam. When the black liquor reaches a concentration of 20 to 23% solids during evaporation, it is sent through soap skimmers where the major portion of this soap salts out, rises to the surface, and is skimmed off. This material is termed "black liquor skimmings" and is the starting material for the manufacture and subsequent processing of crude tall oil.

Production of crude tall oil involves the acidulation of black liquor skimmings or soaps with sulfuric acid at an elevated temperature. The actual mechanics of this production of crude tall oil has been the subject of considerable study, which has resulted in the development of several processes for the conversion of the skimmings to crude tall oil.

Basically the production methods for crude tall oil may be divided into two major classes: a) those which