• **TECHNICAL**

Utilization Potential of *Crambe abyssinica*

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Abstract

Crambe abyssinica can be grown in the principal wheat growing areas of Western U. S. and in the Northern Corn Belt states with yields of 2000 lb of seed/acre. The seed contains 35% oil, in which erucic acid constitutes 60% of the total fatty acids. The erucic acid can be converted by ozonolysis into brassylic and pelargonic acids. It has been estimated that the chemical industry could afford to pay about 7.7¢/lb for the *Crambe* oil, when used for the production of both brassylic and pelargonic acid, assuming an 85% ozonolysis yield for the oil and a sales price of 35¢/lb for brassylic acid and 15¢/lb for pelargonic acid. A higher price could be justified if some of the indicated improvements could be accomplished. The net dollar return/acre has been conservatively estimated to be about $19/acre. The potential market for the *Crambe* crop would probably require the planting of about 65,000 acres.

Introduction

Utilization of the Products from Crambe Abyssinica

THE U.S.D.A. conducts a continuous program on new crops with the objective of developing new and useful crops. It is hoped that this line of research will uncover seeds containing unique oils suitable for industrial use, and noncompetitive with those now in production. Those of particular interest are erucic acid oils from rape, mustard, radish, and other related plants. The unsaturated acids in these oils offer possibilities for cleavage into new dibasic acids for the manufacture of resins, plastics, fibers, and coatings. These crops can be grown in North Central and Northwestern U. S. *Crambe abyssinica* (Abyssinian kale), which is a member of the mustard family, has good crop potential, and the oil extracted from its seed contains 56–60% of erucic acid having the formula:

$$[CH_3(CH_2)_7CH = CH(CH_2)_{11}COOH]$$

Figure 1 represents an oversimplified analysis of the production of brassylic acid from *Crambe abyssinica* oil. The processing would be similar to that presently employed in the oxidative cleavage of oleic acid by ozone:

$$\underset{MW=282.46}{\text{Oleic acid}} + \underset{MW=48}{\text{Ozone}} \longrightarrow \underset{MW = 188.22}{\text{Azelaic acid}} + \underset{MW = 158.24}{\text{Pelargonic acid}}$$

A similar reaction for ozonolysis of the erucic acid obtained from *Crambe abyssinica* seeds has been carried out in the laboratory, according to a reaction which in an oversimplified form proceeds as follows:

$$\underset{\substack{\text{Erucic acid}\\ MW = 338.6}}{CH_3(CH_2)_7CH = CH(CH_2)_{11}COOH} + \underset{\substack{\text{Ozone}\\ MW = 48}}{O_3} \longrightarrow$$

$$\underset{\substack{\text{Brassylic acid}\\ MW = 244.3}}{(CH_2)_{11}(COOH)_2} + \underset{\substack{\text{Pelargonic acid}\\ MW = 158.2}}{CH_3(CH_2)_7COOH}$$

Based upon information received from some of our industrial contacts (1) we have concluded that certain uses exist for the following products and by-products derivable from *Crambe abyssinica* oil:

Brassylic acid of 95% purity. A 95% brassylic acid could probably be sold at about 35¢/lb and at this price it is believed that perhaps 10 million lb annually could be used for polyesters, plasticizers, alkyd resins, lubricants, rubber additives, surface active agents, and others.

Brassylic acid of 99% purity. There appears to be a need for higher mol wt dibasic acids for new fibers with special properties, but for such use polymer grade material of approximately 99% purity (1% or less of monobasic acids) is required. If 99% brassylic acid could be sold in the price range of 30–35¢/lb, which does not appear possible at the present time, a large volume market for fibers requiring perhaps 20 million lb of brassylic acid annually might be developed. It is thought, however, that the 99% polymer grade brassylic acid could be sold at 45–55¢/lb, and at this price we understand that perhaps 5 million lb annually could be sold for new nylon-type fibers having special properties which are not obtainable with the presently available dibasic acids.

Thus, it is estimated that at the prices indicated the total potential market for both 99% and 95% brassylic acid could be about 15 million lb/year.

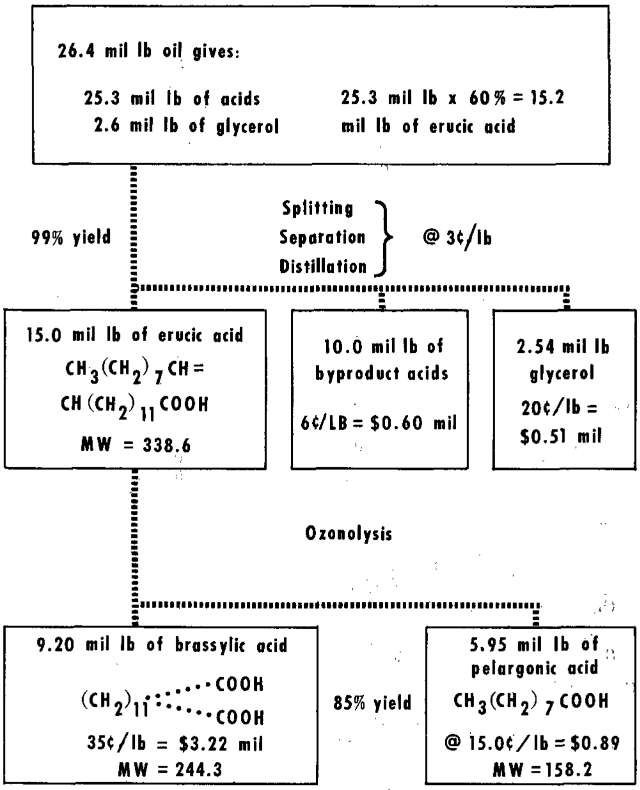

FIG. 1. Production of organic acids from oil.

Assumptions:

Brassylic acid (sales price)	35¢/lb
Splitting, separation and distillation	3¢/lb
Ozonolysis cost (per lb of erucic acid)	10¢/lb
Erucic acid content in oil (based on total acid content)	60%
Ozonolysis yield	85%

TABLE I

Typical Composition of *Crambe abyssinica* oil[a]

Item	Acids in mixed acids: Original	Acids in mixed acids: Erucic removed
	percent	*percent*
Myristic	0.05	0.1
Palmitic	2.0	5.0
Palmitoleic	0.4	1.0
Stearic	0.6	1.5
Oleic	17.9	43.7
Linoleic	9.9	24.2
Linolenic	5.0	12.1
Arachidic	0.8	2.0
Eicosenoic	2.5	6.1
Behenic	1.0	2.4
Erucic	59.1	......
Docosadienoic	0.5	1.3
Tetracosenoic	0.2	0.5
Total	99.95	99.9

[a] Private communication from I. A. Wolff, Northern Utilization Research and Development Division, U.S.D.A.

Coproduct pelargonic acid. About 0.6 lb of pelargonic acid is formed for every lb of brassylic acid produced. A 15 million lb production of brassylic acid would yield about 9 million lb of pelargonic acid annually, which is approx equal to the current consumption (2). Pelargonic esters are expected to find a greatly expanded market in the jet lubricant field (3) and as a blend with azelates to make it competitive with adipates. However, because of the stringent high-temp specifications for military jet lubricants, most of this expansion may be confined to nonmilitary planes. Additional application research will, therefore, be required in order to find new and expanded uses for the pelargonic acid. However, it should be noted that Emery Industries has tripled its production capacity for pelargonic acid. Some of the known uses for pelargonic acid include the following fields: Plasticizers, alkyd resins, vinyl stabilizers, hydrotropic salts, pharmaceuticals, synthetic flavors and odors, flotation agents, insect repellents, and other synthetic chemicals. In some cases mixtures of monobasic and dibasic acids need not be separated but instead might be used directly in the production of polyester plasticizers.

By-product glycerol. Since the present U. S. production of glycerol exceeds 300 million lb/year, the impact of the additional 4 million lb formed in the production of 15 million lb of brassylic acid would be insignificant.

By-product mixed acids. A typical composition of the mixed acids obtainable from *Crambe abyssinica* oil is given in Table I. The acids could probably command a price comparable with that of tall oil fatty acids, 6¢/lb. Since the production of tall oil fatty acids is of the order of magnitude of 200 million lb/year, it is reasonable to assume that it will not be difficult to dispose of this 15 million lb of by-product.

By-product meal derived from Crambe abyssinica seeds. Crambe oil is obtained from *Crambe abyssinica* seed by standard extraction procedures in 35% yield and is intended to be processed as shown in Figure 1. The by-product meal amounts to about 60% of the wt of the seed, and mechanical losses account for the remaining 5%. The by-product meal could probably be sold as fertilizer for about $34/T.

Estimated Cost of Producing Brassylic and Pelargonic Acids from Crambe Abyssinica Oil

We have estimated the gross income, the cost of sales, and the capital investments needed to convert the *Crambe* oil into useful products. These calculations are shown in Table II, at the bottom of which we have indicated the price which we believe the industry could afford to pay for the *Crambe* oil to produce brassylic and pelargonic acids under the described conditions. We have based our calculations on the following assumptions:

Capital investments. We have estimated that a plant capable of processing about 25–30 million lb of *Crambe* oil to yield about 15 million lb of erucic acid for ozonolysis to about 9–10 million lb of brassylic acid (in accordance with the scheme shown in Figure 1) would cost about $6 million. This plant would have facilities for steam generation, splitting, separation, distillation, ozonolysis, and purification for producing the acids.

Cost of production. At an annual production rate corresponding to 15 million lb of erucic acid shown in Figure 1 we have used the following figures:

TABLE II

Effect of Variables upon the Price of *Crambe* Oil

Item	Conservative assumptions	Pelargonic acid price		Brassylic acid price			Erucic acid content 80%	Ozonolysis cost		Ozonolysis yield 90%	Optimistic assumptions
		0¢/lb	25¢/lb	30¢/lb	40¢/lb	55¢/lb		12¢/lb	8¢/lb		
Assumption											
Pelargonic acid sales price ¢/lb	15	0[a]	25[a]	15	15	15	15	15	15	15	25[a]
Brassylic acid (95%) sales price ¢/lb	35	35	35	30[a]	40[a]	55[a]	35	35	35	35	55[a]
Ozonolysis cost ¢/lb	10	10	10	10	10	10	10	12[a]	8[a]	10	8[a]
Ozonolysis yield %	85	85	85	85	85	85	85	85	85	90[a]	90[a]
Erucic acid content %	60	60	60	60	60	60	80[a]	60	60	60	80[a]
Profit before taxes 15%	....	....	....	....	....	....	....	....	....	....	....
Gross income (from 26.4 mil lb of oil):[b]	Mil $	Mil $	Mil $	Mil $	Mil $	Mil $	Mil $	Mil $	Mil $	Mil $	Mil $
Brassylic acid: 9.20 mil lb	3.22	3.22	3.22	2.76	3.68	5.06	3.22[c]	3.22	3.22	3.41[f]	5.36[h]
Pelargonic acid: 5.95 mil lb	0.89	0.00	1.49	0.89	0.89	0.89	0.89	0.89	0.89	0.95[g]	1.58[i]
Byproduct acids: 10 mil lb @ 6¢/lb	0.60	0.60	0.60	0.60	0.60	0.60	0.23[d]	0.60	0.60	0.60	0.23[j]
Glycerol: 2.54 mil lb @ 20¢/lb	0.51	0.51	0.51	0.51	0.51	0.51	0.38[e]	0.51	0.51	0.51	0.38[k]
Total gross income	5.22	4.33	5.82	4.76	5.68	4.06	4.72	5.22	5.22	5.47	7.55
Subtract profit, 15% of $6 mil investment	0.90	0.90	0.90	0.90	0.90	0.90	0.90	0.90	0.90	0.90	0.90
Cost of sales: (gross income less profits)	4.32	3.43	4.92	3.86	4.78	6.16	3.82	4.32	4.32	4.57	6.65
Subtract splitting, separation, and distillation @ 3 ¢/lb	0.79	0.79	0.79	0.79	0.79	0.79	0.64	0.79	0.79	0.79	0.64
Ozonolysis of erucic acid 15 mil lb	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.80	1.20	1.50	1.20
Amount left for oil	2.03	1.14	2.63	1.57	2.49	3.87	1.68	1.73	2.33	2.28	4.81
	¢/lb	¢/lb	¢/lb	¢/lb	¢/lb	¢/lb	¢/lb.	¢/lb	¢/lb	¢/lb	¢/lb
Price of oil	7.7	4.3	10.0	5.9	9.4	14.7	7.9	6.6	8.8	8.6	22.7

[a] Variable assumption.
[b] Based upon analysis in Table I and erucic acid content of 60%.
[c] Based upon 21.2 mil lb of oil containing 80% erucic acid and 20% oleic acid.
[d] 3.81 mil lb.
[e] 1.91 mil lb.
[f] 9.73 mil lb.
[g] 6.30 mil lb.
[h] 9.74 mil lb.
[i] 6.31 mil lb.
[j] 3.78 mil lb.
[k] 1.91 mil lb.

(a) Cost of splitting, distillation, and separation: 3.0¢/lb of *Crambe* oil.

(b) Cost of ozonolysis of erucic acid 10¢/lb including purification of the brassylic and pelargonic acids.

The above cost figures include cost of ozone at 15¢/lb and other raw materials, labor, utilities, depreciation, general overhead, and sales expense.

Profit. Our calculations are based upon the assumption that the industry will operate at a profit margin of 15% on its investment before taxes.

Effect of Future Improvements upon the Crambe Oil Price

The data from Table II are illustrated in Figure 2. The following conclusions can be drawn concerning the effect of possible technological improvements upon the *Crambe* oil price:

Conservative assumption. It can be estimated that under current economic and technological conditions, the industry could pay 7.7¢/lb for the *Crambe abyssinica* oil assuming a profit margin of 15% on its investment before taxes.

Effect of the pelargonic acid selling price. The most important factor affecting the *Crambe* oil price is the selling price of pelargonic acid. The current market price of 25¢/lb for pelargonic acid would actually justify a price of 10¢/lb for the *Crambe* oil. We have, however, considered the possibility that the pelargonic acid price might drop as low as 15¢/lb if its consumption were to exceed 20 million lb/year and if it could be manufactured from octenes and carbon monoxide. In view of this fact, we have based our calculations on the conservative assumption that the pelargonic acid would be sold at a price of only 15¢/lb rather than the current market price of 25¢/lb.

Effect of brassylic acid selling price. The feasibility of the industrial utilization of the *Crambe* oil is also to a major degree dependent upon the selling price of brassylic acid. Thus an increase in the brassylic acid price from 35 to 40¢/lb would raise the price of *Crambe* oil from 7.7 to 9.4¢/lb. It was the opinion of one chemical company that polymer grade brassylic acid could command a price of 55¢/lb, in which case, however, an extra purification step would have to be added.

Effect of the erucic acid content of Crambe oil. The effect of increased erucic acid content upon the *Crambe* oil price is important only if the pelargonic acid can be sold at or near the current market price (25¢/lb) but at the conservatively estimated future price (15¢/lb) the effect of the higher erucic acid content is relatively small. The reason for this is that as the erucic acid of the oil increases, the amount of glycerin yield from the oil decreases. Since the price of 20¢/lb for the glycerin is relatively large compared with 15¢/lb for pelargonic acid, any profits due to an increased production of pelargonic acid are offset by the profits lost due to a decreased glycerin yield.

The erucic acid content of the oil likewise becomes a more important variable in the event that either the glycerin or the by-product acids would be discarded during the operation rather than processed and purified. At a 15¢/lb selling price for pelargonic acid an increase in erucic acid content of the oil from 60 to 80% would only justify an increase in the *Crambe* oil price from 7.7 to 7.9¢/lb. However, at a 25¢/lb price for pelargonic acid the same in-

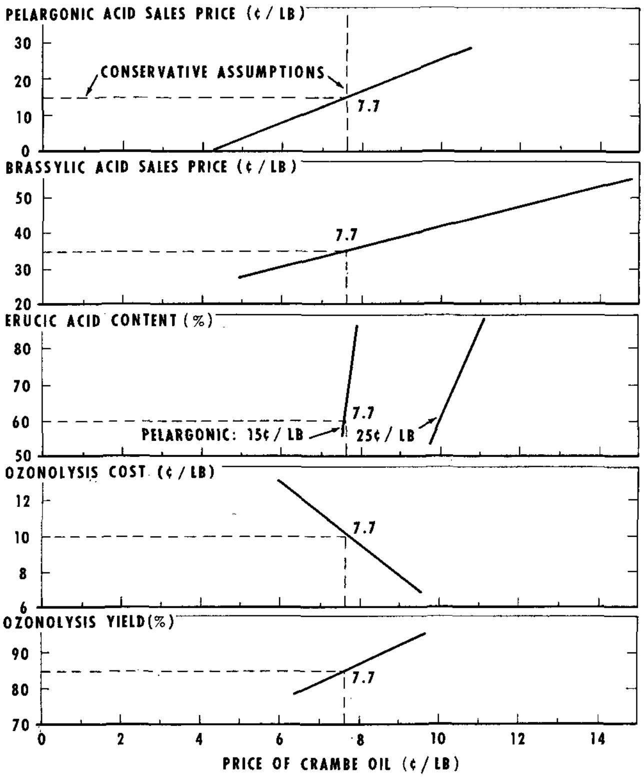

FIG. 2. Possible variations in *Crambe abyssinica* oil price. Effects of various improvements (at 15% profit on investment before taxes).

crease in erucic acid content would allow an increase in *Crambe* oil price from 10 to 10.8¢/lb.

Effect of ozonolysis cost. If the ozonolysis cost of the erucic acid could be reduced from 10 to 8¢/lb, assuming an erucic acid oil content of 60%, a 35¢/lb price for brassylic acid and a 15¢/lb price for pelargonic acid, the *Crambe* oil might command an 8.8¢/lb price (compared with a 7.7¢/lb price at an ozonolysis cost of 10¢/lb).

Effect of ozonolysis yield. If the yield of brassylic and pelargonic acids from erucic acid by ozonolysis could be increased from 85 to 90% using the same costs and prices for the effect of ozonolysis cost, the estimated *Crambe* oil price could be increased to 8.6¢/lb.

Combined effect of all improvements. While it is unlikely that all of the above improvements can be accomplished, we have calculated that the combined effect of the above mentioned improvements would permit the payment of 22.7¢/lb for the *Crambe* oil.

Effect of Future Improvements upon the Dollar Return/Acre from Crambe Abyssinica Crop Production

As indicated in Figure 2, it is estimated that the *Crambe* oil could be sold to the chemical industry for 7.7¢/lb and that higher prices could be justified only if some of the indicated improvements could be effected.

The next consideration is that of determining the cost of producing the oil from the *Crambe abyssinica* crop and estimating the dollar return/acre to the grower.

In Table III we have shown that the net return/acre to the grower of *Crambe abyssinica* crop is about $19/acre. When wheat is grown on the same type of land (value: $100/acre, yield–0.6 T/acre) a net return of about $6/acre is obtained (4). Calculations in

TABLE III
Estimated Net Return/Acre to a Grower of *Crambe abyssinica* Crop

Assumption:	
Yield of oil seed	1.0 T/acre
Amount of oil in seed	35%
Amount of meal	60% (43% protein)
Price of oil	\$154/T (assuming 7.7¢/lb)
Price of meal	\$34.00/T
Processing cost	\$20.00/T
Gross income/acre:	
Oil	0.35 @ \$154/T × 1.0 = \$53.90
Byproduct feed	0.60 @ \$ 34/T × 1.0 = 20.40
Total	\$74.30
Cost of production per acre:	
Farm production cost	\$30.00
Processing cost	20.00
Freight from local elevators to processing plant @ \$5/T	5.00
Total	\$55.00
Net return/acre	\$19.30

Table III are based upon the following information:

Yield/acre. *Crambe abyssinica* planted in Montana on land that had previously been planted in winter wheat gave an average yield of 0.75 T/acre. This land was low in nitrogen and a planting of barley produced about one-half of a normal yield. It is assumed a similar depression in yield occurred with *Crambe abyssinica*. *Crambe abyssinica* has also been grown experimentally in Kansas, Iowa, Indiana, Nebraska, North Carolina, Missouri, Minnesota, Texas, and Wyoming where yields of up to 1 T/acre have been obtained. Thus far, only row planting has been used but with drill planting and further improvements in production practices, we have been informed that a yield of 1½ T/acre would not be overly optimistic (5).

Oil content of seed. The 35% oil content which we have used for the *Crambe* seed was based upon a survey of a number of representative samples and is considered to be a conservative figure (5). Furthermore, we were told that this figure could, in all probability, be raised to 45% through genetic improvement.

By-product meal. At the present time the by-product meal is too toxic to be used as animal feed but could probably be sold as a fertilizer for \$34/ton, which is the current price for castor bean residues. However, we have good reason to expect that the toxicity problem can be solved (6) and that the meal could be sold for feed purposes at \$50/T, which is the current price for soybean by-product feed.

Farm production cost. The figures relating to farm production cost are obviously subject to rather wide fluctuations depending upon location, land value, yield, size of farm, type of soil, and other variables. We have used a figure of \$30/acre at a yield of 1 T/acre (5) and \$35/acre at the higher yield of 1.5 T/acre (7).

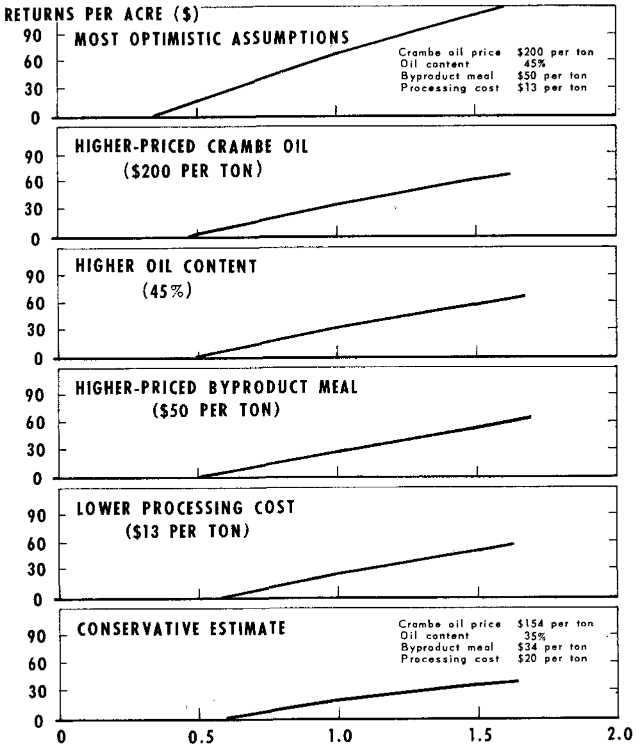

FIG. 3. Dollar return/acre of *Crambe abyssinica* crop. Effects of various improvements.

In Table IV we have calculated the effect of a number of possible improvements, all of which are based upon reasonable future expectations. These data are shown graphically in Figure 3. The net return is conservatively estimated to be about \$19/acre, but could possibly be more than doubled through certain indicated improvements.

Under conservative assumptions, one acre should yield 2000 lb of *Crambe* seed containing 35% of *Crambe* oil which in turn could be processed into about 230 lb of brassylic acid. The annual production of 15 million lb of brassylic acid would probably

TABLE IV
Effect of Possible Improvements upon the Dollar Return/Acre of *Crambe abyssinica* crop

ITEM	Conservative estimate	Lower processing cost	Higher byproduct meal price	Higher oil content	Higher *Crambe* oil price	Most optimistic assumption
Assumption						
Processing cost of *Crambe* seed \$/T	20	13[a]	20	20	20	13[a]
Price for *Crambe* byproduct meal \$/T	34	34	50[a]	34	34	50[a]
Oil content of seed %	35	35	35	45[a]	35	45[a]
Byproduct meal %	60	60	60	50	60	50[a]
Crambe oil price \$/T	154	154	154	154	200[a]	200[a]
Gross income/acre						
Crambe oil	\$53.90	\$53.90	\$53.90	\$69.30	\$70.00	\$90.00
Byproduct meal at stated \$/T	20.40	20.40	30.00	17.00	20.40	25.00
Total	74.30	74.30	83.90	86.30	90.40	115.00
Cost of production/acre						
Farm production cost \$30/acre	\$30.00	\$30.00	\$30.00	\$30.00	\$30.00	\$30.00
Processing of seed at stated \$/T	20.00	13.00	20.00	20.00	20.00	13.00
Freight from local elevator to processing plant @ \$5/T	5.00	5.00	5.00	5.00	5.00	5.00
Total	55.00	48.00	55.00	55.00	55.00	48.00
Net return/acre						
At yield of 1 T/acre	\$19.30	\$26.30	\$28.90	\$31.30	\$35.40	\$ 67.00
At yield of 1.5 T/acre (Farm prod. cost = \$35/acre)	38.95	49.45	53.35	56.95	63.10	110.50
At yield of 0.5 T/acre (Farm prod. cost = \$30/acre)	Loss 5.35	Loss 1.85	Loss 0.55	Profit 0.65	Profit 2.70	Profit 18.50

[a] Variable assumption.

require the planting of about 65,000 acres and result in a gross income of about $5 million.

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Laboratory Sulfonation Methods for Detergent Alkylbenzenes

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Abstract

Laboratory methods are described for evaluation of alkylbenzenes by three different sulfonation techniques: batch oleum sulfonation, continuous oleum sulfonation, and batch sulfur trioxide-air sulfonation. Sulfonation conditions such as temp, mixing, and reaction time are carefully controlled; and the resulting sulfonates are reproducible in quality. Of particular interest is the close control of the sulfonating agent feed rate. In the batch oleum method, this is accomplished by flow through a calibrated capillary under constant head and in the SO_3-air method, by constant rate injection of liquid SO_3 into the vaporizer. In the continuous oleum method, both alkylate and oleum feed rates are kept at desired levels with a duplex positive displacement pump which pumps against spring-loaded ball check valves in the lines to the mixing pump.

Sulfonation data (including solution colors and unsulfonated oil contents of the products) are presented for several commercial detergent alkylbenzenes varying in average mol wt from 241–267. Quality of the alkylbenzene is more critical for the continuous oleum and batch SO_3-air methods than for the batch oleum sulfonation.

Introduction

SINCE THE INTRODUCTION of detergent alkylbenzene sulfonates after World War II, their use has steadily grown to a present level of about 600 M lb/year (10); and they now comprise the largest single type of detergent active production. As their usage increased, improvements in the quality of the detergent alkylbenzenes were continually made to meet the exacting quality standards required by the detergent manufacturers and formulators.

Two of the most important sulfonate quality inspections which concern the detergent manufacturer are unsulfonated oil content and color. Lower unsulfonated oil content means greater sulfonate yield and often better odor and foam performance. Color has become increasingly important because of the consumers' preference for light colored products. Low sulfonate color means savings through reduced requirements in bleaching or in matching uniform colors in dyed products.

Not only the quality of the alkylbenzene but also the method of sulfonation affect the unsulfonated oil and color of the sulfonate. Furthermore, the same alkylbenzene may give a good quality product by one sulfonation procedure but a poor product by another method. Thus, it is imperative that rapid and meaningful laboratory sulfonation tests be available to evaluate detergent alkylbenzenes. This paper presents three laboratory sulfonation methods: batch and continuous oleum sulfonation and batch SO_3-air sulfonation. These methods have proven useful in evaluating differences in alkylbenzenes as well as in developing new alkylbenzenes of the highest quality.

The conditions and reactant ratios given in the methods are those normally used for laboratory evaluations of detergent alkylbenzenes. However, the procedures offer great flexibility as regards temp, reaction times, reactant ratios, and mixing. Usually, the sodium alkylbenzene sulfonates are prepared; but preparation of other salts, such as ammonium or potassium, is equally feasible.

Batch Oleum Sulfonation

Experimental Procedure. Details of the batch sulfonation reactor are shown in Figure 1. Other equipment necessary includes an ice bath, a hot water bath at 180–190F, and two constant temp baths at 120F and at 150F, respectively. The heating or cooling water is circulated through the reactor jacket with a centrifugal pump. Temp, times, and stirring rates are precisely controlled; while the rate of addition of the oleum, which is of particular importance, is maintained by flow through a replaceable calibrated capillary tube under a const head. After completion of the sulfonation step, the reaction mixture is diluted with water to facilitate phase separation of spent acid and sulfonic acid.

Alkylbenzene (1.4 moles) is charged to the reactor and cooled to 40–45F by pumping ice water through the reactor jacket and stirring the alkylbenzene at 900 rpm. Twenty-two per cent oleum (4.5 moles of equivalent SO_3; 3.2/1.0 mole ratio of sulfonating agent/alkylbenzene) is charged to the dropping funnel, the stopcock is opened wide, and the glass stopper is momentarily loosened until oleum covers the delivery tube of the dropping funnel. Oleum will now drop into the sulfonator through the capillary tube under const head and therefore at a const rate. Using a ½-inch long, 1-mm ID capillary tube, the addition