Industrial Uses of High Erucic Oils[1]

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Abstract

Vegetable oils rich in erucic acid have desirable properties for a variety of applications. At present, only a fraction of the potential that exists for commercial exploitation of high erucic oils in the United States is fulfilled with 10 million pounds of rapeseed oil imported annually. Though rape is not a crop in the United States, another member of the mustard family, crambe, has been recommended by the USDA as a practical crop for domestic cultivation. Compared to rapeseed oil, crambe oil is more suitable for industrial use because it consistently contains a higher percentage of erucic acid. High erucic oils, as exemplified by crambe, can be employed as lubricants in continuous steel casting, in formulated lubricants and in the manufacture of rubber additives. Both the hydrogenated oil and derived wax esters have properties comparable to commercial waxes. Useful nitrogen derivatives can be prepared from either the erucic acid or mixed acids from the oil; behenyl amine is used in a corrosion inhibitor, disubstituted amides are effective plasticizers and erucamide is an excellent slip and antiblocking agent for plastic films. Oxidative ozonolysis of erucic acid produces the dibasic acid, brassylic, and the monoacid, pelargonic. Mixed diacids, mainly brassylic and azelaic, can be obtained by ozonolysis of fatty acids from the oil. Alkyl diesters of brassylic, or of the mixed diacids, are excellent low temperature plasticizers. Two new nylons (13 and 1313), which are derived from C-13 difunctional products of erucic acid ozonolysis, contain repeating units that have longer uninterrupted polymethylene chains than other nylons. Moderate melting points and exceptionally low water absorption are a consequence of this structure. The low-melting characteristic is an advantage in adhesive uses and facilitates fluidized-bed coating, molding and extrusion; low moisture affinity contributes to excellent electrical properties and dimensional stability.

Introduction

During the past several years, the USDA has been searching for new crops that can be grown domestically to provide industrially useful products (1,2). For example, there is opportunity for an American crop that can serve as a source of seed oil high in erucic (*cis*-13-docosenoic) acid. Such oils have advantageous properties for a variety of industrial applications. Partial commercial recognition of the versatility of high erucic oils is attested to by the 10 million pounds of rapeseed oil imported annually (3).

According to USDA statistics, rapeseed ranks fifth in the world as an oilseed crop. World production in 1968 was a record 5.86 million tons (4), an increase of over 2.5 million tons per year over the annual average production between 1950 and 1954. Historically, rapeseed has been cultivated for centuries in India, China, Japan and other countries for use as an edible oil and for lighting and lubrication. By the 13th century, it was grown fairly extensively in Europe but was gradually displaced there by other crops until its renaissance following World War II. In 1943 rape was introduced into Canada where it is now grown widely. Canada is the world's leading exporter of rapeseed and now ranks second only to India as the largest producer.

Canadian production of rapeseed has increased annually during the past few years until rape is now the country's fourth largest grain crop (5). Two million acres were seeded to rape in 1969; estimates indicate that 4 million acres were planted in 1970 (6). Prior to 1960, rapeseed was a very minor crop in Canadian agriculture. In less than 10 years, rape has become the "Cinderella" crop of Canada (7).

Most of the oil extracted from rapeseed is used for products such as salad and cooking oils and margarines and shortenings. In anticipation of sustained use of rapeseed oil in foods, Canadian research has developed several types of rape. Canbra, the oil from some of these, is essentially free of erucic acid. We understand production of the erucic acid-free varieties in Canada will be increased as rapidly as possible with the objective of providing some Canbra oil for marketing by 1971 and enough seed for the entire crop in 1972. This will place increased emphasis on an alternative source of a strictly industrial high erucic oil, a possibility which has already caused increased attention to crambe.

Industrial utilization in the United States would undoubtedly be greater if there were a domestic supply of a high erucic oil. At present, crambe (*Crambe abyssinica*) is the most promising source of an oil rich in erucic acid that is suited for domestic cultivation (8,9). Crambe oil resembles rapeseed oil in chemical composition but is more advantageous for chemical use because of its high and more constant erucic acid content.

The glyceride structure of most high erucic oils is unique in that erucoyl groups are esterified almost exclusively to the 1- and 3-positions of glycerol (10–12). Generally, plants that yield high erucic oils do not contain more than 67 mole % of such groups because they seem to lack the proper biosynthetic pathways for attaching erucic acid at position 2. Garden nasturtium (family Tropaeolaceae), which yields seed oil containing 78 mole % erucic acid, is a notable exception (10).

Mixed acids from crambe oil contain 55–60% of erucic acid along with lesser amounts of other fatty acids such as oleic (~15%), linoleic (~10%), linolenic (~7%), eicosenoic (~3%), palmitic (~2%), docosanoic (~2%) and tetracosenoic (~3%). Other physical and chemical characteristics of crambe are shown in Table I in comparison with soybean and olive oils.

Crambe is agronomically adapted for growth in

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TABLE I
Typical Properties of Crambe, Soybean and Olive Oils

Property	Crambe	Soybean	Olive
Specific gravity, 25/25 C	0.911	0.920	0.912
Viscosity, 25 C, Cp	85	50	70
Refractive index, n_D^{25}	1.471	1.473	1.467
Melting point, C	6	—7	2
Iodine value	92	132	85
Unsaponifiables, %	0.6	0.8	1.0
Smoke point, F	520	450	390

most areas of the United States; it is particularly well suited as a summer crop for northern areas and has been grown as a winter crop in southern portions of this country (9,13–17). The possibility of production of two crops per year as far north as Indiana and Illinois has been explored. Such double cropping may become more practical as a result of the release by the Indiana Agricultural Experiment Station of a new variety named "Indy," which matures 10 to 14 days earlier (and has a significantly higher weight of seed per bushel) than the crambe generally grown. An ordinary combine can be used to harvest and thresh crambe. Thus most farmers can produce and harvest this new crop without investing in special farm machinery. Similarly, crambe oil can be removed from the seed by ordinary prepress solvent extraction methods (18).

Like all crucifers, crambe contains thioglucosides which, per se or through transformation products, may adversely affect the quality of the byproduct meal as a livestock feed (19). Much research has been directed toward minimizing this problem through appropriate processing procedures (20,21).

High erucic oils, as exemplified by crambe and rape, can be utilized in several forms: the oil can be used for some applications without further processing, or erucic acid can be obtained from the oil and transformed into derivatives, or the erucic acid can be cleaved at its unsaturated linkage to yield two different acids (brassylic and pelargonic) that can be further reacted to give many useful chemical products. Each of these three categories will be considered separately in the remainder of this article. Although specific references will be to crambe and rapeseed, the discussion should be applicable to other high erucic oils that may be developed in the future.

Uses of High Erucic Oils

Certain vegetable oils find considerable use as lubricants and lubricant additives. It might be expected that the longer polymethylene chains in high erucic oils should lead to improved lubricating characteristics; both rape and crambe oils do in fact exhibit excellent lubricating properties in various applications.

One of the more novel applications of high erucic acid oils as lubricants is in the continuous casting of steel, a European development that has found increasing acceptance by American steelmakers during the last 10 to 15 years. Rapeseed oil is usually mentioned as the material most widely used as a mold lubricant in this process (22,23). At first thought, the use of a triglyceride oil as a mold lubricant may seem surprising since the temperature of the molten steel as it enters the mold is over 2500 F. However, the mold is usually constructed of copper and is water cooled; temperatures on the mold surface are near 400 F. At this temperature high erucic oils remain on the mold long enough to provide efficient lubrication.

The steel industry is now spending $2.1 billion per year in upgrading its total production facilities (24). Assuming most of the modernized facilities will employ continuous casting, the market potential for suitable lubricants is substantial. In cooperation with a major steel producer, crambe oil was tested as a mold lubricant and found superior to rapeseed or any other oil then used for this purpose. Another steel producer found, in tests with crambe, that less oil was required than with rapeseed to give billets of comparable quality. In both trials, crambe produced less smoke and wetted the mold surface better than rapeseed oil. Approximately 4–6 oz of oil is required per ton of steel to achieve adequate mold lubrication.

The present trend is toward larger continuous casting units in which a new inorganic mold lubricant is used. During casting, this powder melts and forms a protective layer over the molten steel that lubricates the mold and also prevents oxidation of the steel. Approximately 50% of the continuous casting operations still use a vegetable oil lubricant (primarily rapeseed oil), but the future for this type of lubricant is uncertain. We understand that some processors have difficulty in handling the new inorganic lubricant and still prefer blown rapeseed oil.

In other areas a high erucic oil, such as crambe, could serve as a spinning lubricant in the textile industry (25), or as a rolling oil in the processing of light gauge steel where oils with low coefficients of friction are desired. As additives, high erucic oils tend to increase the "oiliness" of mineral oil and improve its durability under high speed and high pressure operation. Mineral oil mixtures that contain high erucic oils also form stable emulsions with salt water and have been used as marine lubricants (26). Rapeseed oil is still a significant part of the formulation of lubricants used by British railroads. Crambe oil was tested by a U.S. company and found to be a very worthwhile component in lubricant formulations designed for metal forming operations.

A class of elastic gums can be made by reacting certain unsaturated vegetable oils with sulfur or sulfur derivatives. These products, known as vulcanized vegetable oils, are represented by the familiar art gum eraser (27–29). Vulcanized vegetable oils are widely used for blending with natural and synthetic rubber in rather high proportions to aid in processing and to give soft, highly elastic products that are more resistant to light and ozone. They tend to increase the tolerance for liquid plasticizers, or softeners, in compounded rubber products. These products are made for use in a diversity of rubber formulations from tubing and rubber bands to fabric coatings and automotive products. Rapeseed, soybean and castor bean oils are commonly used for making the various types of elastic gums used in rubber formulations. A vulcanized product made from crambe oil has been commercially evaluated and found to be comparable to, or slightly better than, that made from rapeseed oil.

Hydrogenation of crambe oil yields a glyceride which contains saturated fatty acids and which melts at a higher temperature than the natural product. The hydrogenated triglyceride has a glossy surface and about the same melting point as beeswax (62–65 C), but it is much harder than beeswax (30,31). Liquid waxes can be prepared from the crambe glycerides by sodium reduction to unsaturated fatty alcohols and esterification of these alcohols with crambe acids. Hydrogenation of these liquid wax esters yields a product that melts slightly higher (66–68 C) but is somewhat softer than beeswax (30). Both the solid hydrogenated crambe glycerides and the hydrogenated wax esters have properties that are comparable to many commercial waxes. Neither is as high melting as carnauba (76–84 C) nor as hard.

Derivatives of Fatty Acids From High Erucic Oils

High purity erucic acid is a commercially available chemical intermediate. Probably the most important commercial derivative of erucic acid, erucamide, is presently considered one of the best additives for extruded polyethylene and polypropylene film (32–34). When added to virgin polyolefin resins in low concentrations (ca. 0.1%), the amide functions as an extruder lubricant during processing and thereby speeds and facilitates production (35). During and after processing it exudes to the film surface where it acts as an antiblocking and slip-promoting agent, which prevents films from adhering to one another and allows sheets to slide past each other easily. Erucamide also contributes desirable antistatic characteristics to polyolefins and makes them more susceptible to heat sealing. Oleamide is also used for these purposes and contributes similar properties to polyolefin films. Due to its lower volatility, erucamide is especially recommended where high temperatures are involved; it is the preferred amide for use with polypropylene even though it currently costs twice as much as oleamide. Erucamide is also claimed to improve the finished surfaces of wax-coated paper, giving a more transparent paper of high gloss and improved stick resistance (32); its use in food packaging materials is permitted by U.S. Food and Drug Administration Regulation 121.2509. Production of erucamide in the United States almost tripled from 1965 to 1967 (36).

Saturated, long chain fatty amides such as stearamide are generally employed in the manufacture of durable textile water repellents. The 22 carbon behenamide, when substituted for stearamide in these formulations, is said to give textiles improved and longer lasting water repellency (37).

Fatty amines are widely used as cationic surface active agents in a variety of applications ranging from fabric softeners with bactericidal activity to dispersants and corrosion inhibitors in petroleum products (38). The 22 carbon saturated behenyl amine is a component of a U.S. Navy salt water corrosion preventative; it was the only amine of those tested in the formulation that met the Navy's stringent requirements (39).

Most long chain, fatty nitriles are primarily utilized as precursors for other fatty nitrogen derivatives (38). Eruconitrile can be converted to primary behenyl amine through catalytic hydrogenation. The availability of eruconitrile in developmental quantities has prompted investigation of alternate uses. In exploratory studies, eruconitrile has served as an intermediate in the production of nylon 13 (40).

Several N,N-disubstituted amides of erucic acid and mixed crambe fatty acids have been prepared by amidation of the free acids, or by direct aminolysis of the triglycerides. These amides are effective external plasticizers for poly(vinyl chloride-vinyl acetate) copolymer (PVCA) (41). The best low temperature flexibilities were obtained with either di-*n*-butyl or bis(2-alkoxyethyl) substituents. These derivatives of erucic acid and mixed crambe fatty acids are comparable to a commercial low-temperature plasticizer, bis(2-ethylhexyl) adipate, in respect to low temperature flexibility. In addition, they have vastly superior volatility loss characteristics which overall would make them better plasticizers than bis(2-ethylhexyl) adipate. All but one of the erucic acid derivatives were compatible with the PVCA copolymer and exhibited good low temperature performance and desirable low volatility losses. Derivatives of crambe acids had more limited compatibilities, were more volatile, were not as good in low temperature performance but were somewhat more efficient plasticizers than the corresponding erucoyl amides. Compatibility characteristics were not materially improved in amides prepared from crambe oil which had been partially hydrogenated in the presence of a copper-chromium catalyst (42) to reduce the polyene content to 3.4% without appreciable effect on the monounsaturation.

Products From Oxidative Cleavage of High Erucic Oils

Large quantities of pelargonic (nonanoic) and azelaic acids are presently produced from oleic acid by industrial processes that utilize ozone (43). Pelargonic acid is used for making modern jet aircraft engine lubricants and is now in greater demand than azelaic acid (44,45). Production of brassylic acid from erucic acid (46,47) also yields pelargonic acid as a byproduct, and this could help alleviate the short supply of this monobasic acid without creating a surplus of azelaic acid.

Uses for brassylic acid are many and varied. A novel application is found in the perfume industry where large ring compounds containing 15–17 carbon atoms are often substituted for natural musk to enhance the odor of fragrant components in perfume formulations (48). The cyclic diester of brassylic acid and ethylene glycol, ethylene brassylate, is a well-known synthetic musk used as a fixative in perfumes (49–52).

Various other diesters of brassylic acid with alkyl moieties ranging in size from methyl to decyl have been incorporated into poly(vinyl chloride) (PVC) and evaluated as plasticizers (53). Alkyl side chains up to and including 6 carbon atoms are quite compatible with PVC and have excellent low temperature properties, comparable to the best commercial products. In addition, several of these diesters impart better light stability to the resin. PVC plasticized with bis(2-methylpentyl) brassylate remains flexible to a lower temperature (T_F, −61 C) than PVC plasticized with bis(2-ethylhexyl) sebacate (DOS) (T_F, −57 C) or a number of the other commercial plasticizers.

Dicyclohexyl brassylate has properties that are very similar to those of bis(2-ethylhexyl) phthalate, the most widely used plasticizer in moderate temperature applications. In mixed esters, which consist of two different alcohol moieties esterified to brassylic acid, the cyclohexyl moiety effects a worthwhile improvement in migration and volatility characteristics (54).

Diester plasticizers may also be prepared from the mixed dibasic acids obtained by oxidative ozonolysis of crambe free fatty acids (55). Since the dibasic acids used to make these diesters are mainly azelaic and brassylic acids, we have called this mixture of esters "azela-brassylate" plasticizers. Use of the mixture resulting from ozonolysis of crambe acids has a potential economic advantage in that neither isolation of individual fatty acids before ozonolysis nor

TABLE II

Typical Properties of Nylons[a]

	Nylons				
Property	66	11	12	13	1313
Density, g/ml	1.13–1.15	1.03–1.04	1.01–1.04	1.01	1.01
Melting point, C	255–275	186	180	180	174
Tensile strength, psi	7100–10,200	6950–9250	5530–7420	5600	5210–5700
Elongation at break, %	40–230	180–380	180–285	110	130–290
Modulus of elasticity, psi (X 10^5)	3.8	2.1	1.87	1.3	1.01–1.14
Impact strength (Izod)	1.0–2.0	1.8	1.9–2.1	2.1	2.6
Water absorption, % (at equilibrium, immersed at 20 C)	9.5	1.85	1.26[b]	1.04[c]	0.75[c]

[a] Reference 58.
[b] After seven weeks of immersion.
[c] After five weeks of immersion at 23 C.

separation of dibasic acids afterward is required. A more efficient process for preparing these esters in higher yield (87%) involves oxidative ozonolysis of crambe glycerides followed by acid catalyzed alcoholysis to yield a mixture composed mainly of glycerol, pelargonic acid ester and azela-brassylate diesters (56). The acid catalyst and glycerol are removed by a water wash and the monobasic esters by vacuum distillation. The lower distilling temperature and improved separation give a purer product with less color than was previously realized with the free acids.

All of the azela-brassylate plasticizers that we have prepared with six or fewer carbon atoms in the alcohol moiety are compatible with PVC. Except for a dicyclohexyl ester, all compatible azelabrassylates have excellent low temperature flexibility. Flex temperatures (T_F) of these diesters are only 3 to 10 C higher than brassylates of the same chain length. The 2-methylpentyl ester has the lowest flex temperature (−51 C) of the compatible azela-brassylates and is almost equal to DOS in this respect. The azela-brassylates have somewhat higher volatility than the corresponding brassylates, but show improved migration loss characteristics. Light stability of the azela-brassylates is comparable to, or possibly slightly better than, the brassylates. All compatible azela-brassylates have better light stability than DOS.

A major potential market for brassylic acid is in the production of a new, longer chain polyamide, nylon 1313. The monomers for this new nylon are brassylic acid itself and 1,13-diaminotridecane, the 13-carbon diamine made from it. To make the diamine, brassylic acid is reacted with ammonia under dehydrating conditions to give brassylic acid dinitrile (1,11-dicyanoundecane) which is converted to the diamine by catalytic hydrogenation (45). Diamine and diacid monomers are combined in stoichiometric proportions to form the nylon salt which is readily converted to the polyamide by melt polymerization. Monomers for nylon 1313 have sufficiently low volatility that pressure is not required during the initial stages of polymerization as is necessary for the lower nylons.

This new polyamide contains repeating monomer units with longer polymethylene chains than in commonly available nylons. A consequence of this structure is a moderate melting point that results in easy fabrication of this polymer for use in molding and extrusion, adhesives and fluidized bed coating operations. When applied as a fluidized bed coating, the bond between the nylon 1313 and the metal is stronger than the cohesive strength of the nylon itself. Nylon 1313 can be injection molded without the use of excessive temperatures, pressures or dwell times. It has very low water absorption and moisture regain, low mold shrinkage and high dimensional stability, good flow properties in molding applications, excellent electrical properties and excellent resistance to attack by chemicals (57). Typical properties are shown in Table II (58). Processes for the production of nylon 1313 were developed by the Southern Research Institute under contract with the USDA. Under a new contract, pilot plant production of nylon 1313 is now under study.

A related product that is similar in properties to nylon 1313, but has not been so thoroughly studied, is nylon 13. One successful route to nylon 13 starts with eruconitrile. Oxidative ozonolysis of the nitrile yields a mixture of pelargonic acid and the cyano acid, 12-cyanododecanoic acid (40). This mixture is then esterified with methanol and vacuum distilled to separate the two esters. Catalytic hydrogenation of the cyano ester (methyl-12-cyanododecanoate) then produces an amino ester which is hydrolyzed to the amino acid monomer, 13-aminotridecanoic acid. The cyano group is reduced as the cyano ester, rather than the cyano acid, because the acid precipitates out on the catalyst. Melt polymerization is the preferred method of polymerizing the monomer to nylon 13. Typical properties of nylon 13 are shown in Table II (58).

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