Report of the Literature Review Committee

Annual Review of the Literature on Fats, Oils and Detergents. Part III.

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H. BOOK REVIEW

PRODUCTION PROCESSES

VEGETABLE AND ANIMAL OILS AND FATS

Reviews were published on basic engineering concepts in the oils and fats industry (M. Lancin, *Riv. Ital. Sostanze Grasse, Sympos Issue* 194 (1962); Recent developments in vegetable oil processing equipments (H. Watanabe, *Yukagaku 12*, 549 (1963); New developments in the unit processes used in oil mills and refineries (C. Von Erhardt, *Grasas y Aceites 15*, 17 (1964); Degumming, refining, discoloration and deodorization of soybean oil (A. V. Romero and F. R. Ayerbe, *Rev. Franc. Corps Gras. 11*, 3 (1964); Supply of oilseeds, oil milling and solvent extraction (H. D. Howard, *Rept. Progr. Appld. Chem. 47*, 153 (1962) and statistics of olive oil production in Italy and the world (F. Zito, *Riv. Ital. Sostanze Grasse, Sympos.* Issue 103 (1962).

The production of animal fats by melting techniques (H. P. Kaufman and K. D. Mukherjee, *Fette Seifen Anstrichmittel 66*, 385 (1964), and the current status of production and use of edible meat fats (J. W. Woerfel, *JAOCS 41*, 4 (1964) were also reviewed.

A detailed description of the machinery produced in Italy for the pretreatment and pressing of olives was given (G. Jacini and C. Carola, *Riv. Ital. Sostanze Grasse 41*, 290 (1964). The various aspects of Italian olive oil industry were presented (O. T. Rotini, *Ibid. 38*, 532 (1961). Cantarelli reported the economic factors connected with olive oil production (C. Cantarelli, et al., *Ibid. 40*, 463 (1963). A relationship between the size of the kernels of olive and physico-chemical characteristics of the oil was established (G. Petruccioli, *Olearia 17* (3-4), 112 (1963).

The technology of sunflower seed processing in the Poltava fatty-oil plant was discussed (A. A. Lesyuis et al., *Sb. Statei O Robotakh Ukr. Nauchn.-Issled Inst. Maslozhir Prom. Kharkov* (4-5) 7 (1959, 1961). Solvent extraction, drying of fatty substances, bleaching, deodorization, distillation, fractionation, esterification of fatty acids, concentration and purification of glycerol and drying by atomization were described (R. Francais, *J. Chem. Eng. Data 17*, 453 (1962).

Importance of climate, plant breeding and economics to production of oilseeds in Canada was discussed (H. R. Sallans, *JAOCS 41*, 215 (1964). Some problems in improving tropical materials like palm oil, palm kernel, peanuts utilized by the oil milling industry in the United Kingdom were described (E. S. Hiscocks and W. D. Raymond, *JAOCS 41*, 224 (1964).

Substantial deterioration of quality occurred during storage of Nigerian palm kernels. Lipolytic micro-organisms were found to be partially responsible for the deterioration (E. A. Simmons and A. Sheridan, *J. West African Sci. Assoc. 8*(1), 18 (1963). The quality of the oil obtained from rapeseeds dried with flue gases at 120–40C was as good as that of oil obtained from fresh ones (A. Jakubowski et al., *Tluszcze i Srodki Piorace 6*(2), 59 (1962). No change was observed in the oil content or free fatty acid content of safflower seed stored for 210 days. However, the free fatty acid content of dehulled kernel increased 20-fold. Refined safflower oil stored for 700 days showed a 3-fold increase in free fatty acid content (S. A. Ahmed et al., *Oilseeds J.* (Bombay) *16*(5), 1 (1963).

A patent for inhibiting color deterioration of refined soybean oil by incorporation of an alkali salt of a polybasic acid such as sodium or potassium citrate or tartarate during deodorization was obtained (Nisshin Oil Mills, *Japan 5,005/63*). Cyclopropene acid content of cottonseed oil was found to decrease effectively in the presence of aluminum sillicate catalyst at elevated temperature (A. J. Deutschman, Jr., et al., *JAOCS 41*, 175 (1964). Pokorny observed that the degree of refining accomplished on low quality coconut oil prior to its hardening did not affect the temperature range over which the hardened oil softens and melts. However, deodorization was found to narrow the melting range significantly (J. Pokorny and G. Janicek, *J. Inst. Chem. Technol. Prague 6-1*, 313 (1962).

A process for the manufacture of a fat-containing dried dairy produce which was a free-flowing granular material characterized by high wettability and dispersibility in cold water was patented (J. M. McIntire and C. C. Loo, *U.S. 3,120,438*). A dry powder containing 80% butterfat could be manufactured by spray-drying a suitable mixture of milk constituents and other ingredients (P. M. T. Hansen, *Australian J. Dairy Technol. 18*, 79 (1963).

Formulae for estimating the drying, extraction and storage capacity needed in a plant processing olive oil "Orujo" were developed (B. Espuny, *Lipidos 22*, 113 (1963).

EXTRACTION

Reviews were published on oil production by solvent extraction (H. P. Kaufmann and R. Gueldenpfennig, *Fette Seifen Anstrichmittel 65*, 671 (1963); solvent extraction of fatty materials (K. Maebashi, *Yukagaku 12*, 561 (1963); and extraction of olive oil by the "Extraoil" method (D. D. Arino, *Lipidos 23*, 34–36, 77–80, (1963).

Witz et al., described a modern plant for the processing of cottonseed and other oil-bearing materials, which recovered two thirds of the oil by prepressing the conditioned raw material followed by countercurrent extraction of the presscake with hexane for complete recovery of the oil (H. J. Witz and

W. B. Hendrik, *Chem. Eng. 71*(18), 48 (1964). Prepress solvent extraction of *Crambe* seed oil was successfully carried out on a commercial scale (Anon., *Chem. Eng. News 42* (9), 50 (1964). In the prepress solvent extraction of sunflower oil, experiments on settling of miscella verified the possibility of decanting in an industrial plant (V. E. Ovcharenko, *Sb. Statei O Rabotakh Ukr. Nauchn.—Issled Inst. Maslozhir Prom., Kharkov (4–5)*, 19 (1963). A rectangular water filter tank with a conical bottom was used to separate the grist particles from ligroine miscella (A. S. Mochalov, *Mekhaniz i Artomatiz Proizv. Protosessov v Maslozhir Prom. Moscow Sb.* 72 (1961).

Buzi used a new type of filter element made from polyvinyl chloride in pressing olives (C. Garocci Buzi, *Sostanze Grasse 38*, 443 (1961). The Sima-Baglioni system for extracting oil was found to yield 6% more oil than older extraction methods in use for olive oil. (Anon., *Grasas y Aceites 14*, 147 (1963). The application of filtration extraction to rapeseed was discussed. Cooking the crushed seed without addition of water and at temperatures not exceeding 220C produced a satisfactory oil and good extraction efficiency (J. R. Reynolds and C. G. Young, *JAOCS 41*, 63 (1964). Consecutive extraction of thoroughly crushed oilseeds with water and application of impulse rendering to the vegetable oil industry appeared to be commercially feasible (V. V. Beloborodov, et al., *Maslob.-Zhir. Prom. 30*(8), 5 (1964). A method for obtaining by exclusively physical and mechanical steps a high grade coconut oil from coconut cream was patented (D. M. Birosel, *U.S. 3,106,571*). Extraction of fat from swine flesh involved hydrolysis of protein substances contained in the tissue with solutions of NaOH and Na_2CO_3 followed by centrifuging to separate nonfat substances from fat (S. G. Liberman and V. P. Petrovskii, *Tr. Vses. Nauchn.—Issled Inst. Myasn. Prom. 13*, 3 (1962).

Defatting of peanuts on a pilot plant scale was carried out to obtain data for cost calculations and to investigate practical methods of desolventizing extracted peanuts (J. Pominski, et al., *JAOCS 41*, 66 (1964). Large differences were found in the maximum pressure and length of cycle used in the hydraulic press extraction of olive oil in several commercial plants (J. M. Martinez *Grasas y Aceites 14*, 162 (1963). The effects of stepwise predisgestion of cottonseed meals with various solvents followed by pressing out the miscella, on the rapidity of extraction were investigated (I. M. Ismailov, *Maslob-Zhir. Prom. 30*(5), 10 (1964).

A high fatty acid content or changes in the phosphatide content of the oil had no effect on adhesion of oil on materials for oil extraction. However, moist-heat treatment of the meal decreased oil adhesion (K. E. Leont'evskii and M. A. Chudnovskava, *Tr. Vses. Nauchn.—Issled Inst. Zhirov 22*, 5 (1961). The use of aqueous surfactants for economical commercial manufacture of fats and oils was described (M. Mathieu, *Journees Inform. Acides Gras Derives*, Paris, 75 (1961). Surfactants added to ground olive pastes affected the quality and quantity of oil recovered by solvent extraction, pressing and centrifuging (J. M. Martinez Moreno and J. Ruiz Cruz, *Grasas y Aceites 14*, 257 (1963). Data on the solvent-binding power of cottonseed, sunflower seed, soybean meal as influenced by the size distribution, the porosity of particles, the oil and moisture content and the weight and density of the meal was presented (I. V. Gavrilenko and I. M. Ismailov, *Maslob-Zhir. Prom. 29*(9), 16 (1963). In the extraction of palm oil in continuous presses the pulp-to-nut and matte-to-nut ratios were dependent on the variety of palm fruit (Alex Wolvesperges, *Oleaqineux 18*(11), 717 (1963).

Extraction of soybean press-cake with acetone gave better extraction and better quality meal than with ligroine. Further, it improved the ease of hydrogenation of the oil (N. K. Nadirov and R. V. Bobrinetskaya, *Izv. Vysshikh Uchebn. Zavedenii, Pishchevaya Tekhnol 4*, 58 (1963). Oil cake with low oil content was obtained by extracting the soybean containing less than 5% moisture, with 4 times its weight of 96% alcohol for 2 hr in a wormscrew extractor (F. A. Vishnepol'skaya, *Tr. Vses. Nauchn.—Issled Inst. Zhirov 23*, 131 (1963). Rice bran oil with a low acid value was obtained by extraction in two steps using methanol and hexane or benzene (Hiroshi Inoue and T. Noguchi, *Yukagaku 13*, 206 (1964).

A polarographic method for continuously determining the concentration of fatty miscella was developed (V. M. El'gort and I. V. Karyakina, *Izv. Vysshikh Uchebn. Zavedenii, Pishchevaya Tekhnol. 4*, 149 (1963). Nickel, aluminum (LA6), bronze (B4417), bronze (B7) and brass (M58) had satisfactory corrosion resistance for use in solvent extraction plants (Czeslaw Mikitiuk, *Tluszcze i Srodki Piorace 6*(3/4), 128 (1962).

A mathematical-statistical study of the effects of the ratio of benzene to prepressed sunflower grist and the moisture content of the incoming extractable material on the fat content of the extracted grist was made (N. G. Eshchenko, *Maslob-Zhiv. Prom. 30*(8), 9 (1964). A theoretical-mathematical treatment of the regularities in the process of filtering of sunflower miscella was given (R. I. Spinov, *Maslob-Zhir. Prom. 30*(5), 5 (1964).

DEGUMMING AND REFINING

A patent for continuous degumming of vegetable oils pertained to introducing a mixture of vegetable oil and an aqueous degumming agent under high pressure into a continuous centrifugal separator in which the mixture would be separated into degummed oil and wet gums (N. W. Myers, *U.S. 3,134,794*). The optimum conditions for degumming were found to be 4–5% H_2O with 15–20 min stirring at 75–80C for cottonseed and 4–5% H_2O with 20–30 min agitation at 50–60C for peanut oil (K. S. Iyer and K. S. Murti, *Indian Oilseeds J. 7* (4), 299 (1963). Treatment with 0.05 to 0.3% hydrochloric acid for 15 min at 20–30C was found to be the best for degumming linseed oil (R. Guillaumin and N. Drouhin, *Rev. Franc. Corps Gras 10*, 671 (1963).

A simple, easily controlled process for continuous caustic refining of crude cottonseed oil miscella in a two-stage system was described (L. S. Crauer and H. Pennington, *JAOCS 41*, 656 (1964). Optimum conditions for refining corn oil in a miscella state were 100–150% excess alkali, 8% alkali and 10–20% miscella at a temperature of 65C (D. Barcza and J. Peredi, *A Novenyolajes Haztartasi Veghip. Kut. Inst. Kozlemen* 75 (1962). Acid vegetable oils were neutralized by extracting a mixture of oil and stiochiometrically calculated amount of NaOH or Na_2CO_3 solution, successively with three different solvents such as trichloroethylene, hexane and EtOH. This procedure prevented the adsorption of neutral oil on the foots (*Ital. 643,056*). Crude vegetable oils were refined by neutralizing with NaOH followed by agitation for 1–2 hr at 40–60C with a hydrocarbon solvent such as hexane which formed a solution having a specific gravity lower than the soapstock. The two phases were centrifugally separated (*Ital. 639, 905*).

Hydroxy forms of anion exchange resins EDE-10 and AN-2F were effective in removing gossypol from refined cottonseed oil miscella in benzene (N. V. Rizaer, et al., *Uzbeksk Khim. Zh. 8*(1), 44 (1964). Pro-oxidant metals in crude soybean oils in acetone or n-hexane solutions could be removed effectively by passing through columns of a strong cation exchange resin (A. Vioque et al., *JAOCS 41*, 785 (1964). Some safety hazards in solvent plant and miscella refining operations were enumerated (G. C. Cavanaugh, *JAOCS 41*(10), 4 (1964). Olive oil was deacidified with IMAC-S-5-30 ion exchange resin. Regeneration of the resin was achieved by treatment with aq.-alcoholic NaOH solution (M. DeFelice and V. Bolcato, *Riv. Ital. Sostanze Grasse 39*, 125 (1962). Refining of sesame oil with Amberlite IRA-400 was patented (N. Kamada et al., *Jap. 10*, 475).

Refining of vegetable and animal oils and fats was accomplished by treatment with Na_2SiO_3 solution at 40–80C (I. Meister and Pal Nanasi, *Hung. 151, 055*). Soybean oil was neutralized by treatment with 1–2.5% of a 10% Na_3PO_4 solution at 50C followed by treatment with 16C Bé Na OH at 75–80C. The soap was removed by spraying hot water at the surface of the oil and allowing it to settle for 3 hr (L.C. Hedon and M. G. Zurera, *Span. 283*, 666). Soybean oil was degummed and refined in one step using a nitric acid solution. The oil so treated could be easily bleached and deodorized (R. Guillaumin and N. Drouhin, *Rev. Franc. Corps. Gras 10*, 463 (1963). Oil obtained by pressing or extraction was refined at 55C with 1.5% crystalline sodium acetate and 1.5% of 30% hydrogen peroxide and the mixture was stirred vigorously for 30 min with simultaneous raising of the temperature to 90C. Then the oil was sprayed with hot 5% sodium chloride solution after discontinuing stirring (E. Hlavsa and A. Prikryl, *Czech. 110, 110*).

Oils with less than 1.5% free fatty acid were neutralized with 160% excess of hot Na_2CO_3 solution at 90C with stirring for 0.5 hr. For oils with free fatty acid greater than 1.5% refining was done using the above conditions but under vacuum (E. Atanasova et al., *Khranitelna Prom. 8*(12), 11 (1959). Addition of 0.5% tera-sodium pyrophosphate during conventional alkali refining of tobacco seed oil reduced the refining loss by 30% (B. R. Reddy et al., *Research Industry* (India) *8*, 227 (1963).

Best results were obtained when high acid cottonseed oils obtained from low grade seeds were treated with urea prior to alkali refining (A. S. Sultanov et al., *Tr. Vses. Nauchn.—Issled Inst. Zhirov 23*, 280 (1963). Deacidification with urea could be used in place of complicated alkali refining for prerefining of high acid cottonseed oils. The method was also applicable to oils containing large amount of saturated acids with some linoleic acid but not to oils with large amount of linoleic acid with little saturated acids (N. V. Vengerova and A. I. Petrova, *Tr. Vses. Nauchn.—Issled Inst. Zhirov 23*, 273 (1963). Oils of low and medium acidity could be deacidified by treating with urea at 40C in the presence of 30% water with agitation for 2 hr (J. Zajic, *J. Inst. Chem. Tech. Prague 7-2*, 181 (1963).

Vegetable oils were deacidified by extraction with aqueous mixture of solvents like acetone (B. Foresti, *Ital. 606, 971*). Over 95–98% of the fatty acids were extracted from high acid oils by 7-fold extraction with 96% EtOH at 30–40C (J. Zajic, et al., *Sb. Vysoke Skoly Chem—Technol Praze Oddil Fak. Potravinareske Technol. 4*, 253 (1960).

Both p-aminosalicycilic acid and p-aminobenzoic acid were equally efficient when used at 0.6% level, in completely removing gossypol from cottonseed oil. (J. Patwari and S. D. Thirumala Rao, *Indian J. Technol. 1*, 435 (1963). In the presence of phosphatides the rate of formation of reaction products of gossypol and O-aminobenzoic acid derivative was faster and filtration and dehydration of the precipitate was easier (V. P. Rzhekhim and A. B. Belova, *Tr. Vses. Nauchn.—Issled Inst. Zhirov 23*, 210 (1963).

A method for removing major portion of the unsaponifiable material from Vernonia anthelmintica seed oil to obtain an improved quality oil was described. Trivernolin was also obtained from the seed as a major end product in yields of 55-60% of the weight of the oil present (C. F. Krewson and W. E. Scott, *JAOCS 41*, 422 (1964). During refining of citran oil 97% of lipochromes and 96% β-carotene were lost (J. Slawinski et al., *Roczniki Technol. Chem. Zywnosci 9*, 139 (1962).

Nosti observed that refining losses were unrelated to the moisture content of the sunflower oils but were approximately equal to 1.91 (% free fatty acids) + 1.16 (M. Nosti, *Grasas Y Aceites 14*, 210 (1963). There was no difference between results obtained for refining rape oil by batch process or by continuous deLaval process (A. Ruthkowski et al., *Roczniki Technol. Chem. Zywnosci 10*, 155 (1964). A description of the operating performance of Podbielniak extractor for refining of vegetable oils was given (L. S. Queirolo, *Riv. Ital. Sostanze Grasse*, Sympos. Issue 161 (1962). Refining of oils was reviewed (C. B. Barrett, *Rept. Progr. Appl. Chem. 47*, 158 (1962).

A simple and cheap procedure for refining commercial sardine oils was presented (D. P. Sen et al., *Food Sci.* (Mysore) *12*, 189 (1963). Fish oil with acid No. of 12.4 was neutralized by passing through a column of EDE-10P resin containing 63% H_2O (M. M. Ol'Shanova and G. V. Frolova, *Rybn. Khoz 40*(2), 85 (1964).

BLEACHING

Published reviews included current oil bleaching technology (T. Nakazawa, *Yukagaku 12*, 69 (1963); active bleaching earth and alumina gel for oil industry (*Ibid.* 483 (1963) and the raw materials and processes employed in the manufacture of bleaching earths (K. P. Koegler, *Fette Seifen Anstrichmittel 65*, 834 (1963). A seminar on bleaching earths and active carbons covering their production and economics, utilization, standards and specifications, and geology and minerology was held (*Council of Scientific and Industrial Research*, India).

The effect of physical and chemical properties of bleaching clay on its performance was discussed (A. D. Rich, *JAOCS 41*, 315 (1964). The physico-chemical and bleaching properties of some of the natural bleaching earths from the Far East for bleaching soybean oil were studied. Some of these earths after acid activation were found to be suitable for the purpose (N. K. Nadirov, and D. V. Sokol'skii, *Tr. Vses. Knof. Alma-Ata 81* (1963).

The effects of acidity, moisture content, temperature and time on the bleaching efficiency of earths from different sources was discussed (H. P. Koegler, *Fette, Seifen, Anstrichmittel 65*, 940 (1963). A mixture of bleaching earth and citric acid or sodium or potassium polyphosphates removed Fe from sunflower oil more efficiently than the earths alone. However, earth polyphosphate or earth alone was equally efficient in removing copper (K. Taeufel and F. Linow, *Ernachrungsforschung 8*(3), 345 (1963). The order of deodorization power for bleaching soybean oil was active clay > active carbon > active alumina gel. Active carbon and clay had no selectivity for tocopherol, iron and soap. Dried alumina chiefly adsorbed tocopherol and wet alumina adsorbed iron and soap. With each adsorbent, a linear relation was found between the peak value of the color reversion and the tocopherol content of the oil (I. Harada et al., *Nippon Nogei Kagaku Kaishi 35*, 212 (1961). At 95C rapid bleaching of palm oil was achieved with activated bleaching earths. The decomposition of the hydroperoxides was found to be responsible for the discoloration which was due to the removal of carotenoids (F. D. Tollenaar and H. Hockman, *Fette Seifen Anstrichmittel 66*, 430 (1964). Treatment of crude rice bran oil with H_2O_2 gave a better yield of the bleached oil than treatment with fuller's earth (T. Suchiya, et al., *Tokyo Kogyo Shikensho Hokokou 56*(2), 69 (1961). Chromophoric power of oxidized fats having nonremovable color, was enhanced by the action of bleaching earth. The formation of the color depended on the nature and amount of the oxidized chains present in the oil to be bleached and of the nature of the bleaching earths used (M. Lachamp and M. Naudet, *Rev. Franc. Corps Gras 11*, 205 (1964).

No detectable amount of polymerization or triene conjugation occurred on bleaching refined cottonseed oil with either activated alumina or with sulfurous acid treated alumina, although insignificant amounts of diene conjugation and *trans* isomerization occurred (J. C. Kuck et al., *JAOCS 41*, 101 (1964).

A continuous process for bleaching animal and vegetable fats and oils consisted of feeding a mixture of bleaching earth and oil at less than 100C into a series of interconnected tubes in which were placed direction-of-current nozzles spaced and designed to convert laminar flow to a turbulent flow (Rolf Peter, *Ger. (East) 27*, 174).

Among the mathematical relations proposed for the interpretation of adsorption phenomena, that of Langmuir permitted determination of theoretical limits of decolorization under experimental conditions from the physical constants (P. Fontana and O. Colagrande, *Riv. Ital. Sostanze Grasse 39*, 180 (1962). In the bleaching of olive oil the experimental points fit well on the straight line Langnuir relationship up to a certain value of the color reading, above which they began to deviate appreciably (P. Fontana and O. Colagrande *Ibid. 41*, 246 (1964).

An apparatus with enclosed filters for recovering fatty material from used bleaching earth, using petroleum solvent or hexane as extractant was described (F. Muscari-Tomajoli, *Ibid. 38*, 336 (1961).

DEODORIZATION, WINTERIZATION AND FRACTIONATION

An apparatus for deodorizing oils and similar liquid materials consisted of a column through which the oils and spent fluid would run countercurrently followed by mixing of the oil with fresh fluid in a plurality of compartments arranged in series (J. A. DeSmet, *U.S. 3,129,076*). The design and general operation of a deodorizer employing a frothlayer for continuous deodorization of fats and oils were discussed (L. A. Gel'perin et al., *Tr. Vses. Nauchn.—Issled Inst. Zhirov 24*, 133 (1963).

Oils and fats were deodorized with reduced Ni-silicate or reduced Ni-Mgo-silicate catalyst by drying with H_2 or desulfurized town gas (Shigeki Yonezu, *Japan 11*, 134). The current oil deodorizing technology was reviewed (A. E. Williams, *Ind. Aliment 2*, 51 (1963).

Oils low in linolenic acid were obtained through winterization and fractionation of soybean oil hydrogenated to iodine value (I. V.) between 85 and 110 (C. D. Evans et al., *JAOCS 41*, 260 (1964). A process for winterizing a glyceride oil in the absence of a solution in a solvent, involved lowering the temperature of the oil to 50–35F to solidify at least a portion of the higher melting glycerides and continuously introducing, at a predetermined rate, a stream of the chilled oil and solids to a zone of centrifugation (T. H. Little, *U.S. 3,145,223*).

Mixtures of solid and liquid fatty acids from olive oil could be separated almost quantitatively by double fractionation with symmetrical dichloroethane at −35C (G. B. Martinenghi, *Olearia 17*, 187 (1963). Animal and vegetable fats and oils having an initial I. V. of about 40 to 70 were selectively hydrogenated to decrease the I. V. by not more than 10 and then were fractionated by single or mixed solvents into trisaturated, disaturated and monounsaturated, monosaturated and diunsaturated, and triunsaturated glycerides (Y. Toyama et al., *U.S. 3,105,844*).

The graphical representation of the phase diagram of glyceride fractionation by Co- and counter-current systems was discussed (E. Sambuc, *Rev. Franc. Corps. Gras. 11*, 319 (1964). The application of liquid-liquid extraction theory to glyceride fractionation was evaluated (*Ibid.*, 326 (1964).

A plant built by Loders and Nucoline Ltd., England, for obtaining selected glycerides by continuous solvent fractional crystallization was described (Anon., *Food Process. Packaging 33*, 9 (1964).

Molecular distillation of a mixture of glycerides prepared by esterification of the tall oil fatty acids showed that the unsaponifiable compounds were concentrated in the first distillate fraction (M. Antila et al., *Suomen Kemistilehti 35B*, 84 (1962).

HARDENING

A reaction vessel assembly suitable for small scale catalytic hydrogenation using a specially shaped vibrating stirrer which produced vigorous agitation of the reaction mixture was described (M. J. D. Low et al., *JAOCS 41*, 433 (1964).

No isotopic discrimination was observed when catalytic reduction of methyl oleate was carried out at atmospheric pressure and 40C temperature. Under conditions described tritium and deuterium could be used to study the mechanism of hydrogenation without significant isotopic effects (E. D. Bitner et al., *JAOCS 41*, 1 (1964). Extensive exchange of deuterium for carbon bonded hydrogen was found to take place during catalytic reduction of methyl oleate with gaseous deuterium. The authors found no simple correlation between isomerization and migrating tendencies of catalysts for double bonds (W. K. Rohwedder et al., *Ibid., 41*, 33 (1964). The position of oleoyl group in the triglyceride molecule was not a factor in the rate of hydrogenation or isomerization during hydrogenation of olive oil (H. V. Turner et al., *Ibid. 41*, 413 (1964).

The speed of isomerization was about four times the speed of hydrogenation of the double bonds during selective hydrogenation of rapeseed oil under industrial conditions (A. Jakubowski and Z. Kowzan, *Rev. Franc. Corps. Gras 11*, 67 (1964). Geometrical isomerization of double bonds proceeded to a greater extent than the addition of hydrogen during commercial selective hardening of vegetable oils (A. Jakubowski, *Prumysl. Potravin 15*, 397 (1964). During industrial hardening of rapeseed oil, acids with 2–3 double bonds were hardened almost exclusively and only small amounts of saturated acids were formed. However, *cis-trans* isomerization prevailed over hydrogen addition (J. Pokorny and J. Ruzicka, *Prumysl. Potravin 15*, 392 (1964). *Cis-trans* isomerization took place to a greater extent in erucic acid than in oleic acid during hydrogenation of rapeseed oil fatty acids. But erucic acid hydrogenated more rapidly than oleic acid (V. Koman, *Prumysl. Potravin 15*, 394 (1964). During hardening of vegetable oils to a hard fat, hydrogenation and isomerization proceeded at approximately the same rate. However, where hydrogenation was used to produce soft, plastic fats, hydrogenation rate exceeded the rate of isomerization (J. Pokorny, *J. Inst. Chem. Tech.* (Prague) *7-1*, 125 (1963).

Partial hydrogenation of a mixture of methyl *cis* 6-, *cis* 9- and *cis* 12-octadecenoates indicated that the double bonds in these positions were hydrogenated at the same rates. However, double bonds near the carbonyl group hydrogenated faster than that near the methyl group when hydrogenation was done under high isomerization conditions (R. R. Allen *JAOCS 41*, 521 (1964).

Rao et al., described a method of preparation and storage of active catalyst for hydrogenating castor oil (H. S. Rao et al., *Indian J. Technol. 2*(1), 21 (1964). Preparations of Raney Ni rapidly lost their activity when stored in absolute ethanol due to formation of acetaldehyde by the residual aluminum. Catalysts thus deactivated by acetaldehyde could be reactivated to a greater degree of activity than that possessed originally by treating with acetic acid. However, the activity of the original Ni catalyst could be preserved to a greater extent by storage in dioxane instead of ethanol (H. V. Turner et al., *JAOCS 41*, 213 (1964). Natural bleaching earths such as tripoli of the Far East could be used not only for bleaching but also as carriers for Cu-Ni catalysts for hydrogenation of soybean oil (N. K. Nadirov, *Zh. Prikl. Khim. 37*(3), 654 (1964). Preparation of copper-chromium manganese catalyst to produce low-melting hardened oils by hydrogenation at 130–200C under a hydrogen pressure of 1 to 10 atmospheres for ½ to 2 hr in the presence of about 2% catalyst was described (K. Kuwata et al., *U.S. 3,129,235*).

The rate and selectivity of hydrogenation of cottonseed oil with Raney nickel catalyst increased with increase in temperature. However, with ceramic-nickel catalyst the rate increased slightly but selectivity remained constant. Plutonium was more active than palladium. However, selectivity in both cases increased with increase in temperature (V. N. Rozhkova and A. L. Markman, *Uzbeksk. Khim. Zh. 8*(2), 38 (1964). A triple use of nickel-chromium catalyst for hydrogenation of sunflower oil in a Vishnevskii autoclave at 100–180C and 0.6–6 atmosphere hydrogen pressure did not decrease its specific activity or selectivity (D. V. Sokol'skii and K. Zhubanov, *Met i Khim Prom. Kazakhstana, Nauchno—Tekhn. Sb. 6*, 100 (1962). Raney nickel catalyst was more selective than copper-nickel catalyst and the hydrogenation could be carried out at temperatures 79–90C lower than those used with copper-nickel catalyst resulting in a product of better quality and lower cost (A. P. Nechaer, *Tr. Mosk. Tekhnol. Inst. Pishchevoi Prom.* No. 20, 8 (1963).

A survey of nickel, plutonium, and palladium catalysts prepared on silicas, aluminas and molecular sieves indicated that the nature of the support contributed considerably to selective hydrogenation of soybean oil. Nickel-molecular sieve catalysts provided both high selectivity and low *trans* isomer formation (C. H. Riesz and H. S. Weber, *JAOCS 41*, 464 (1964). Certain plutonium, palladium and rhodium catalysts demonstrated higher selectivity ($S_L = 2.4–2.7$) for hydrogenating linolenic component in soybean oil. Nickel catalysts generally showed selectivities below $S_L = 2.0$ although skeletal nickel achieved higher values (C. H. Riesz and H. S. Weber, *Ibid. 41*, 400 (1964). Platinum catalyst was less selective than nickel catalyst when methyl linoleate was hydrogenated at 140C and atmospheric pressure (C. R. Scholfield, et al., *Ibid. 41*, 615 (1964). High degree of selectivity was found when homogeneous catalytic hydrogenation of sorbic acid was carried out with pentacyanocobaltate II (A. F. Mabrouke et al., *Ibid. 41*, 153 (1964). Iron-pentacarbonyl was demonstrated to be an effective homogenous catalyst for the reduction of polyunsaturated fats (E. N. Frankel et al., *Ibid. 41*, 187 (1964). The use of an oil with C_{16}–C_{18} fatty acids to slurry the catalyst for hydrogenation of coconut oil produced 5–7% fully hydrogenated triglycerides with a melting point of 60C (J. Pokorny and G. Janick, *J. Inst. Chem. Tech. (Prague) 5-3*, 185 (1961).

Sokol'skii et al., observed that the use of solvents affected the kinetics and mechanics of reaction and increased the rate of reactions by 4–5 times in the hydrogenation of cottonseed oil with palladium-plutonium (3:1) catalyst at 50C. Similarly, the addition of carrier like carbon for the catalyst enhanced the reaction rate by 4–5 times over that obtained without carrier (D. V. Sokol'skii and L. I. Zueva, *Tr. Vses. Konf. Alma-Ata.* 66 (1962). Hydrogenated fats were prepared by low temperature hydrogenation of vegetable oils in solvents using 3:1 palladium-plutonium on a carrier of activated carbon or aluminum silicates as catalyst (D. V. Sokol'skii and L. Zueva, *USSR 1663,700*). Increasing the molybdenum content of the Raney nickel catalyst to 10% in the hydrogenation of cottonseed oil in absolute methanol at different temperatures and atmospheric pressure increased the activity of the catalyst. However, addition of cobalt up to 5% did not affect the activity and further addition decreased the activity of the catalyst (D. V. Sokol'skii and N. S. Samsonova, *Maslob.—Zhir. Prom.* 37 & 7), 12 (1964). Application of ultrasonic waves during hydrogenation of olive oil in a solvent phase notably accelerated the reaction but reduced the selectivity (G. Saracco, *Chim. Ind.* (Milan) *43*(11), 1394 (1963) when sunflower and olive oils in acetone solution were hydrogenated on Raney nickel (1–3%) or palladium on carbon (0.01%) it was possible to check the selectivity of hydrogenation by measuring the potential of the catalyst in acetone and by observing the changes in the fatty acid content of the intermediate hydrogenation products (L. S. Golodova and E. A. Pod'yacheva, *Tr. Vses. Konf. Alma-Ata,* 109 (1962).

The catalytic re-forming process for producing hydrogen for the vegetable oil and other industries was reviewed (B. J. Mayland et al., *JAOCS 41*, 26 (1964).

Hladik and Zajic concluded that optimal conditions for hydrogenating castor oil were 0.5% Ni catalyst at 160C and atmospheric pressure (J. Hladik and J. Zajic, *Sb. Vysokeskoly Chem.—Technol. Praze, Oddil. Fak. Potravinareoke Technol. 4*, 241 (1960). Castor oil was hydrogenated to a product melting at 79.8C with I.V. 14.1, Sap. No. 184.8 and OH value 133 using nickel catalyst at 150C under 1.2 atmosphere pressure for 5 hr (C. Kaczanowski and A. Jakubowski, *Tluszcze i Srodki Piorace 6*(3/4), 125 (1962).

An increase in *trans* acids with increase in temperature was observed during hydrogenation of sunflower oil at atmospheric pressure with 0.3–2% nickel catalyst. Reaction rates at various temperatures were calculated and the activation energy for the reaction was estimated at 17.4 Kcal. (J. Zajic and J. Preiningerova, *J. Inst. Chem. Tech.* (Prague) *7-1*, 135 (1963). A decrease in the conjugated linoleic acid with increase in the time of hydrogenation was observed when rape oil was hydrogenated at 160C with 0.3% nickel or copper-nickel catalyst with a 20 liter hydrogen flow per minute per kilogram of oil (I. Kaganowicz, *Tluszcze i Srodki Piorace 6*(2), 71 (1962).

Two patents on hydrogenation included a process for fatty materials using nickel on silica gel catalyst, temperature from 50–240C and hydrogen pressure ranging from atmospheric to 4000 psig (W. H. Flank, *U.S. 3,123,627*), and a continuous process in which the glycerides were passed through a bed of solid catalyst made up of nickel and sulfur on silica support at 100–400F with hydrogen pressures from 10–150 psig (F. W. Kirsch, *U.S. 3,123,626*).

Hydrogenated rapeseed oils varied in composition reflecting varying selectivity of the commercial hydrogenation processes (A. Jakubowski et al., *Prace Inst. Lab. Badawczych Przemyslu Spozywczego 13*(1), 41 (1963). Nickel was removed best from hydrogenated oils with 0.25% bleaching earth plus 0.02% citric acid (A. Rutkowski et al., *Zeszyty Nauk. Wyzszej Szkoly Rolniczej Olstynie 13*(3), 397 (1962).

A mathematical derivation was developed to determine the selectivity of catalysts for selective hydrogenation of linolenic acid in soybean oil to counteract the undesirable flavor reversion properties of soybean oil (C. H. Riesz and H. S. Weber, *JAOCS 41*, 380 (1964). Applicability of a small analog computer to a study of the kinetics of hydrogenation was presented. Analog computer techniques facilitated the empirical method of trial and error, successive approximation and curve matching and permitted the prediction of the composition of the reaction mixture as a function of reaction time (R. O. Butterfield et al., *Ibid. 41*, 29 (1964).

To obtain a hydrogenated product without reversion of taste and odor, the deodorization of pre-refined whale oil before hydrogenation was recommended (F. G. Gladkaya et al., *Maslob—Zhir. Prom. 29*(11), 43 (1963).

PARTIAL ESTERS AND INTERESTERIFICATION

Three new methods for production of mono- and diglycerides were described. Mono- and diglycerides were produced in high concentration by direct esterification using p-toluenesulfonic acid catalyst and with continuous removal of water of esterification by azeotropic distillation (A. T. Gros. and R. O. Feuge, *JAOCS 41*, 727 (1964). Glycerolysis of oleostearine with NaOH catalyst as 205C for 2 hr yielded a product containing 49% monoglyceride. One recrystallization from hexane, CCl_4, $CHCl_3$ or trichloroethylene gave a product having 77–93% monoglyceride (M. H. Bertoni et al., *Rev. Argent. Grasas y Aceites 5*, 43 (1963). In the production of monoglycerides from refined animal and vegetable fats by glycerolysis the use of cyclohexanone instead of furfural showed good results (S. Tsuda and N. Wada, *Osaka Furitsu Kogyo—Shoreikau Hokoku 25*, 49 (1961).

Substantially complete random rearrangement of glyceride esters containing less than 0.1% free fatty acids was effected with an alkali catalyst. At the end of the reaction citric acid or $H_3\ PO_4$ was added to inactivate the catalyst and to split the soap formed (*Can. 672, 715*). Milk fat was rearranged using selected times, temperatures and catalyst concentrations to yield a product resembling butter. The catalyst concentration had more influence on the hardness than did reaction time or temperature (J. B. Mickle et al., *J. Dairy Sci. 46*, 1357 (1963). The smallest amount of EtONa to transesterify a mixture of 35% lard and 65% rape oil was 0.15% by weight. The reaction was completed in 2 min at 85C and in 1 min at 115C (C. Kaczanowski and A. Jakubowski, *Tluszcze i Srodki Piorace 7*(2), 67 (1963). Fatty acids were esterified with MeOH or BuOH in a specially designed apparatus. When H_2SO_4, or Me—$C_6H_6SO_3H$, was used as catalyst the reaction time was less than 1 hr while catalysts like Cl SO_3H, HCl or H_3PO_4 needed about 5 hr (Hermann Stage, *Chemiken—Ztg. 87*(18), 661 (1963).

Interesterification of fats and oils was reviewed (E. Servent, *Lipidos 23*, 81 (1963).

FAT SPLITTING

An apparatus for continuous splitting of fats was described (I. M. Torbin and E. E. Fainberg, *Maslob—Zhir. Prom. 30* (5), 34 (1964). Splitting of fat was carried out in 80 ft towers operating at 700–750 lb/sq in. pressure and at 460–500F with high pressure steam (H. W. Ladyn, *Chem. Eng. 71*(7), 106 (1964).

Twitchell reagents were uneconomical for splitting of nigerseed, tobaccoseed, safflower, pongam, cottonseed, peanut, chaulmoogra and mahua oils. But dodecylbenzene sulfonic or alkylnaphthalene sulfonic acid catalysts at concentrations of 1–2% gave 90% splitting of all oils in 8–10 hr (C. S. P. Rao et al., *Indian J. Technol. 1*(12), 457 (1963). In the Twitchell method of fat splitting, 80–90% split occurred in about 12 hr with Duolite C-20 cation exchanger and 83% split was obtained with $H_2\ SO_4$. However, the fatty acids obtained with resin catalyst had a much lighter color. Further, the resin could be regenerated (S. D. T. Rao and C. S. P. Rao, *Chem. Age* (India) *14*, 476 (1963).

BY-PRODUCTS

A process for preparing full fat soybean flour for human consumption by ''Extrusion-Cooking'' method was developed (C. G. Mustakas et al., *JAOCS 41*, 607 (1964). Methods for utilizing soybean oil phosphatides in soapstocks were reviewed (F. Ramos, *Grasas Aceites 14*, 171 (1963). Extraction of cottonseed flake containing 5–8% moisture with nonpolar solvent followed by polar solvent decreased the free gossypol content to less than 0.1%. Increasing the temperature to 200–300F for 0.5–2.0 hr at 10–20% moisture level also decreased the gossypol content (W. W. Meinke and Raymond Reiser, *U.S. 3,124,461*). An oil cake containing a maximum of soluble protein and free sugar and a minimum of free and bound gossypol was obtained by extracting with a mixture of liquid and gaseous carbon tetrachloride (V. P. Rzehin et al., *Trudy Uniiz 23*, 70 (1963).

Tocopherol concentration would be commercially feasible only from tocopherol rich dehydration distillate of oil deodorization (H. Niewiadomski and Drozdowski, *Roczniki Technol. Chem. Zywnocsi 9*, 57 (1962). Nitrogen solubility index, optical density of aqueous extracts and reducing sugar content correlated with the protein quality of processed mustard seed (J. E. McGhee et al., *JAOCS 41*, 359 (1964). The economics of the recovery of glycerol obtained by saponification of animal fats was discussed (Mark Krnic, *Kem. Ind. (Zagreb) 12* (4), 231 (1963).

The Annual Review of Literature will be continued in October

• *New Literature*

STURDILITE PRODUCTS, INC., manufacturers of laboratory and industrial furniture, has described its expanded line of modular furniture in its 1965 catalog, No. 563. (919 North Michigan Ave., Chicago, Ill.)

PARR INSTRUMENT CO., has issued their new Calorimeter Catalog, No. 65-1, which lists combustion bombs, calorimeters, automatic calorimeter control systems and calorimeter accessories. (211 Fifty-third Street, Moline, Illinois.)

GALLARD-SCHLESINGER CHEMICAL MFG. CORP. has issued "Organic and Inorganic Research Chemicals," Catalogue No. 5. (580 Mineola Ave., Carle Place, L.I., New York 11514.)

• *Names in the News*

Two staff members of Atlas Chemical Industries' technical center—Paul Becher (1954) research scientist, and William C. Griffin (1954) associate director of produce development—have been named joint recipients of the 1964 Literature Award of the Society of Cosmetic Chemists. The award consists of a prize of $1,000 and a scroll, and is presented annually at the society"s Spring Technical Meeting in New York City.

J. T. Goodwin, Jr., has been appointed Director of the Department of Chemistry and Chemical Engineering at Southwest Research Institute. For the past seven years he served as Vice-President for Research of the Corn Industries Research Foundation, Inc.