

SOME PROBLEMS IN THE SYNTHESIS OF THE
MONO-UNSATURATED FATTY ACID DIMERS*Barbara Rybczyńska, Wiesława Siemaszko*

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Industrial production of the mono-unsaturated fatty acid dimers has been started only about 30 years ago. These compounds have appeared to be very valuable intermediates for the manufacturing of the numerous products of wide application. They are mainly used in the plastic, synthetic adhesive, and paint industry. Metallic salts of dimerized fatty acids are used as emulsifiers in the emulsion polymerization, and also as the lubricant additives. Dimers in ester form are used as low viscosity lubricants, and as stabilizers of the synthetic resin emulsions. Polyester resins based on fatty acid dimers are used as raw materials for the manufacturing of the temperature and chemical resistant laminates. Products of the reaction of isocyanates with the polyesters of fatty acid dimers are very good raw materials for the manufacturing of the polyurethane foams. Polyamides of dimers are used as the hardeners of the epoxy resins.

Such wide application of the dimerized fatty acids is the result of their unique properties and the manufacturing of these products under the industrial scale [1-3].

Fatt acid dimerization consists in the union of the two molecules. Irrespective of the method of dimerization reaction yields a mixture of dimers, trimers and higher polymers. Composition of the reaction mixture depends upon the type of raw material, the method of dimerization, and the process parameters (Table 1). Dimers (trimers) higher polymers ratio has a primary effect on such physical properties of product as viscosity, refractive index etc.

Unsaturated fatty acids, chiefly oleic and linoleic acids, are used as raw materials in the industrial scale production.

According to M.J.A.M. den Otter ionic dimerization of oleic acid consists in the interim formation of the linoleic and stearic acids from

the two molecules of the oleic acid in the result of the hydrogen transfer reaction. Then a molecule of the linoleic acid reacts with the another molecule of the same acid or with the molecule of the oleic acid. Dimers containing the cyclohexene ring represented by the following structures are formed:

These products may contain one or two ethylenic bonds.

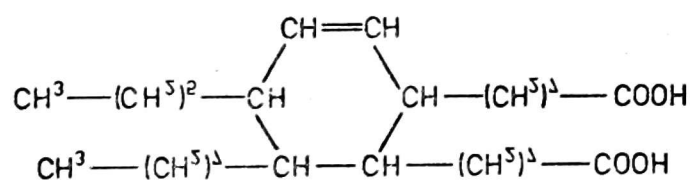
Some examples of the dimerization of the oleic acid are given in Table 2.

Products obtained in the dimerization process consist of monomers, dimers, higher polymers and some products of side-reactions. These are chiefly linear and cyclic hydrocarbons with straight and branched chains and CO_2 . Dimerization process never precedes with the stoichiometrical yield, and the yield depends upon the method of dimerization and process conditions. Achieving the maximum yield at the lowest higher polymer content is the main problem in search for the optimal dimerization process conditions. An important problem is also achieving products of defined structure.

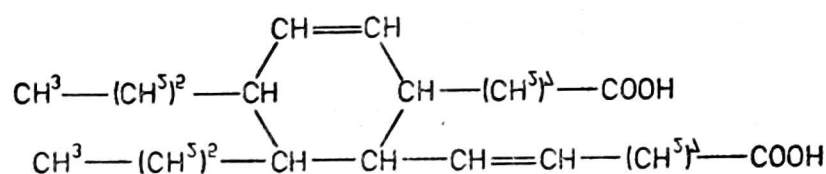
In the work carried out in the Institute of Industrial Chemistry the dimerization of the technical grade oleic acid (Table 3) was performed by ionic method with the natural acid-activated clay catalyst containing less than 20% of oxides of trivalent metals (Al_2O_3 , Fe_2O_3). $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$ ratio varied from 7 to 9. Composition of the clay is given in Table 4.

Dimerization process carried out at 180-260°C, under the pressure of 10-20 atmospheres with, or without water was studied in our work. After the process had been completed gaseous and volatile products were released. Gaseous products¹ contained:

CO_2 16-20% by volume



or



¹ Researches carried out in Analytical and Physicochemical Laboratory. Institute of Industrial Chemistry.

Table 1

Type and structure of oleic and linoleic acid dimers relating to the method of dimerization

Fatty acids	Method of dimerization	Dimer structure	Number of unsaturated bonds in molecule	Particular dimer type content, %	Reference
Oleic	thermal	1. monocyclic: cyclobutane and cyclopentane rings,	0	30	5
		2. linear	1	40	
		3. linear	2	30	
	ionic	monocyclic: cyclohexene ring with saturated and unsaturated side chains	a.v. 2		6
	radical	linear with tow content of cyclic products	2	about 100	7
Linoleic	thermal	1. monocyclic: cyclohexene ring with saturated and unsaturated side chains	2	27.5	8
		2. bicyclic: two cyclohexene rings or one cyclohexene and one cyclopentene ring	2	50.0	
		3. tricyclic: one cyclohexene ring, others unknown	2	22.5	
	ionic	1. monocyclic: benzene ring with saturated and unsaturated side chains		50	9
		2. bicyclic with benzene ring, structure of others	2	39	
		3. tricyclic rings unknown		11	
		radical	linear	4	7

CO 1.8-3.9% by volume

O₂ 0.23-0.4% by volume

Unsaturated hydrocarbons with molecular weight of 70 and 96 volatile products consisted of water, and straight and branched hydrocarbons.

Organic impurities, which condensated out with water vapour, are easily biodegradated and do not need any preliminary chemical treatment. Obtained product was separated from the catalyst on a pressureless fliter. Filtrate consisted of a mixture of dimers and monomers. Its characteristics was following:

Solidifying point, °C	19-25	at 45°C, cP	90
Viscosity at 25°C, cP	240	at 80°C, cP	25

Table 2

Results of the dimerization of unsaturated fatty acids carried out by various methods

Fatty raw material	Method of dimerization	Process conditions				Characteristics of the residue after distillation				
		time, h	temp. °C	pressure, at.	type and amount of catalyst %	yield %	dimer %	trimer %	L.V.	
Oleic acid	thermal	65	280	1	—	—	—	—	—	
Oleic acid	ionic	4	240	—	montmorillonite, 4%	—	—	—	—	
Oleic acid	ionic	4	240	10	water, 2% montmorillonite, 4%	45	82	18	114	
Oleic acid	two-stage ionic	4	160	1	alkali, 1.7% on clay	55	88	12	—	
Oleic acid	ionic	4	230	7	BF ₃ , 1% montmorillonite, 4%	50	70—75	25—30	—	
Oleic acid or methyl oleate	radical	48	130	1	butyl peroxide, 7.5%	—	—	—	91.7	
Methyl oleate	radical	48	130	1	butyl peroxide, 6%	25.15	72	28	59.4	

Table 3

Composition of the oleine used in the dimerization process

Fatty acid	%, by weight
C ₈	0.1
C ₁₀	0.1—0.2
C ₁₂	0.2
C ₁₄ : 0	1.7—1.8
C ₁₄ : 1	0.7—0.8
C ₁₄ : 2	0.2—0.3
C ₁₅	0.2—0.4
C ₁₆ : 0	7.7—8.2
C ₁₆ : 1	5.4—5.6
C ₁₆ : 2	0.6
C ₁₇	1.2—1.6
C ₁₈ : 0	1.5—2.5
C ₁₈ : 1	68.9—69.4
C ₁₈ : 2	6.0—6.5
C ₁₈ : 3	1.0
C ₂₀ : 1	2.0—2.2
Unidentified matter	6.8—0.9

Table 4

Composition of clay used in dimerization process

Main components	%, by weight
SiO ₂	61.1—65.5
Al ₂ O ₃	15.4—17.1
Ignition losses (including water)	11.5—14.9
Moisture content (at 105°C)	3.0—9.0
pH of 2% solution	3.9—5.8

Monomeric acids were eliminated by the thin film distillation. They consisted of C₁₀-C₂₀, saturated and unsaturated fatty acids with high content of various types of isomers. These acids can be dimerized with the yield of 12%, and dimers with quite different properties than oleic acid dimers are obtained.

In the course of the experiments we have succeeded to assess the effect of several factors, which have an important influence on the dimerization of the oleic acid.

Water content has a positive effect as well on the catalyst activity as on the protection of raw material against decarboxylation. Water shows also the stabilizing effect on the degree of polymerization. Ap-

plication of the clay catalyst with less than 20% of the trivalent metal oxides enables to obtain products with low trimer content.

Dimerization carried out within the higher range of temperature produced an effect of an increase of the raw material reaction, but simultaneously the decarboxylation process took greater part, giving an increase of the trimer and unsaponifiable matter content. Carrying the process within the low range of temperatures gave an increase of the time of the reaction and a decrease of yield. One the first method of the fatty acid dimerization was the thermal polymerization. Actually this method is modified by the application of the catalyst and elevated pressure. Fatty acid dimers can be also obtained by ionic method carried out in the presence of an acid-activated silica-alumina catalyst and, by the combination of these two methods.

Typical thermal polymerization consists in the prolonged heating of the fatty acids at 250-350°C in the atmosphere of an inert gas. In the result of the reaction a mixture of polymers of various molecular structure is obtained. Final product contains more than 30% of higher polymers.

Among the ionic methods of fatty acid dimerization a method with montmorillonite type clay catalyst is mostly used. In this method fatty acids or their esters are heated at 250°C for several hours in the presence of the catalyst clay and water, under the pressure of 15 atmospheres.

Pressure in the autoclave depends upon the process temperature and water content.

Characteristics of the technical grade dimers obtained under the

Table 5

Physicochemical properties of dimers prepared from oleine and from recycled fatty acids

	Dimers prepared from oleine	Dimers prepared from recycled fatty acids
Acid value	170—190	148—158
Saponification value	192—200	162—190
Iodine value	80—100	41—75
Monomer content, %	8—8	13.5—18.5
Unsaponifiable matter content, %	0.5—1.5	1.5—4
Viscosity, cP at 25°C	5500—8500	14700—24000
35°C	1400—2100	2800—4300
80°C	200—300	300—550

optimal conditions from the technical grade oleic acid and from the recycled fatty acids is shown in Table 5.

Dimers obtained from the recycled fatty acids had higher viscosity, lower iodine value and higher unsaponifiable matter, monomer and trimer content. These properties indicate on the lower quality of these products.

Fatty acid dimers obtained from the technical grade oleic acid in a single-stage process consisted of:

Monomers	less than 5 ⁰ /o,
Dimers	more than 85 ⁰ /o,
Trimers	less than 10 ⁰ /o.

CONCLUSIONS

Single-stage dimerization of the oleic acid, carried out by ionic method with the activated clay catalyst containing less than 20⁰/o of trivalent metal oxides, enables to obtain the low viscosity dimers with the iodine value similar as for the raw material. Dimer to trimer ratio does not exceed 0.1.

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PROBLEMY SYNTEZY DIMERÓW KWASÓW TŁUSZCZOWYCH JEDNONIENASYCONYCH

Streszczenie

Dimery kwasów tłuszczowych jednonienasyconych, obok dimerów kwasów wielonienasyconych, znajdują coraz szersze zastosowanie przemysłowe. Zależnie od metody ich otrzymywania charakteryzować się będą różną budową. Przeprowadzono badania otrzymywania dimerów metodą jonową z użyciem naturalnego glinokrzemianu aktywowanego kwasem. Chemizm tego procesu jest złożony. Podstawę stanowi reakcja przeniesienia wodoru. W wyniku reakcji powstają dimery zawierające pierścień cykloheksenowy w cząsteczce. Obok dimerów powstają produkty dalszej polimeryzacji — trimery i produkty ubocznych reakcji, węglowodory liniowe i cykliczne z łańcuchami prostymi i rozgałęzionymi. Węglowodory dają się oddzielić od dimerów w czasie przebiegu procesu technologicznego, natomiast oddzielenie trimerów jest sprawą trudną. Zastosowane warunki syntezy pozwoliły na maksymalne obniżenie zawartości niepożądanych trimerów.

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ПРОБЛЕМЫ СИНТЕЗА ДИМЕРОВ МОНОНЕНАСЫЩЕННЫХ ЖИРНЫХ КИСЛОТ

Резюме

Димеры мононенасыщенных жирных кислот находят, наряду с димерами полиненасыщенных кислот, все более широкое применение в промышленности. Они характеризуются разной структурой, в зависимости от метода их получения. Проводились исследования по получению димеров ионным методом при использовании природного алюмосиликата активируемого кислотой. Химизм этого процесса сложный. Основой является реакция переноса водорода. В результате реакции образуются димеры содержащие циклогексеновые кольцо в молекуле. Наряду с димерами образуются продукты дальнейшей полимеризации — тримеры и продукты побочных реакций, линейные и циклические углеводороды прямыми и разветвленными цепями. Углеводороды могут отделяться от димеров в ходе технологического процесса, отделение же тримеров затруднительно. Примененные условия синтеза позволили максимально снизить содержание нежелательных тримеров.