ZESZYTY PROBLEMOWE POSTĘPÓW NAUK ROLNICZYCH 1981, z. 211

TRANSFORMATIONS OF FATTY ACIDS DURING THEIR DISTILLATION

Włodzimierz Zwierzykowski, Halina Szeląg, Barbara Orzęcka, Eleonora Ledóchowska

Institute of Organic and Food Chemistry and Technology, Gdańsk Technical University, Poland

Waste fatty acids and rapeseed oil fatty acids were subjected to batch fractional distillation under diminished pressure on a laboratory scale. The influence of distillation parameters on the transformations of fatty acids was investigated.

Quantitative changes of unsaponifiable matters, hydrocarbons, cyrbonyl compounds, oxy acids and polymers were determined during distillations which were carried out in the atmospheres of nitrogen, air, areated and deaerated steam.

Fatty acids distillation caused their considerable losses and formation of compounds which deteriorate the obtained distillates.

There is no much evidence in literature of fatty acids during their distillation [4, 5] and there are studies presented concerning the improving of applied apparatus to obtain the best fractionation [6-9]. But results are to be found on determination of thermal transformations of oils and fatty acids heated at temperature of 250-300°C at neutral gas or air atmosphere [1, 2].

One of the main reactions occuring during the distillation is the decarboxylation of fatty acids with formation of ketons as well as saturated and unsaturated hydrocarbons.

The polymerization of unsaturated fatty acids occurs and compounds of various weight are formed [3].

Besides of above mentioned processes there occur oxidation type transformations by radical mechanism, as the autooxidation. Such processes results in aldehydes and ketons. Hydroperoxides from the first stage of autooxidation can next undergo polymerization. As an effect the polymer of great oxygen contents can be formed.

In our work we tried to study the influence of the distillation parameters on the quantitative changes of individual compounds formed during that process.

EXPERIMENTAL PART

The rapeseed oil and waste fatty acids were distilled. The gas chromatography analysis of the raw materials was carried to establish their acidic composition.

The following chemical characterization was determined: saponification value, neutralization value, iodine value, peroxide value and the contents of unsaponifiable matters, hydrocarbons, carbonyl compounds, oxy acids and polymers.

Carbonyl compounds were determined by spectrophotometric method. The polymers content were established by column, thin layer and gas chromatography.

Table 1

The characterization of raw fatty acids

Chemical characterization	Waste fatty acids	Rapeseed oil fatty acids
Neutralization value	188.9	172.1
Saponification value	215.8	183.3
Iodine value	51.6	103.5
Peroxide value	33.0	12.0
Oxyacids contents (%)	0.2	0.2
Unsaponifiable matters contents (%)	3.1	0.7
Hydrocarbons contents (%)	18.3	15.0
Carbonyl compounds contents (%)	0.8	0.9

Table 1 gives the characterization of raw fatty acids. No presence of polymers was observed in crude fatty acids. Fatty acids distillations were performed in all glass periodic apparatus by controlled pressure. The parameters of the distillation column are given in Table 2.

Series of experiments with variable parameters were carried in investigate the transformations of fatty acids during the distillation process. The distillations of rapeseed oil fatty acids and waste fatty acids were made using air, nitrogen, deaerated steam and nondeaerated steam atmospheres.

Three different pressures were maintained to every of above men-

Table 2

The characterization of the laboratory column applied to fatty acids distillation

Static hold up (ml)	100.0
Dynamic hold up (ml)	40.0
Total hold up (ml)	140.0
Vapour velocity in the column $\left(\frac{g}{s\ cm^2}\right)$	2.91
Amount of theoretical plates	6.0

tioned gas. First running, the distillate and residue were collected. After distillations of fatty acids the analysis of received products were carried out. The products were analysed analogously to the raw material but the fatty acids balance was calculated for each process.

Table 3

Composition of rapeseed oil fatty acids distilled at deaerated steam

Fatty acids	Rapeseed oil fatty acids	First running	Distillate	Residue	Total fatty acid percentage
$C_{14:0}$	0.1	0.1	—	—	0.1
$C_{16:0}$	3.4	1.2	0.7	0.1	2.0
$C_{16:1}$	0.3	0.2	0.1	—	0.3
$C_{18:0}$	1.3	0.2	0.7	—	0.9
$C_{18:1}$	12.6	1.8	9.2	0.3	11.3
$C_{18:2}$	12.1	1.7	7.5	—	9.2
$C_{18:3}$	9.5	0.9	4.0	—	4.9
$C_{20:1}$	10.3	—	9.5	0.3	9.8
$C_{22:0}$	50.4	—	41.0	3.4	44.4
$\Sigma C < C_{14:0}$	—	0.9	—	—	0.9

The boiling point of fractions: first running 185—190 °C, distillate 190—229 °C, p = 2 mm Hg.
The amount of crude fatty acids was 600 g.
The quantity of steam used during the distillation was 4.2 g.

Table 3 gives the composition of fatty acids in distillation fractions and in raw rapeseed oil fatty acids. The distillation was carried at deaerated steam and a pressure of 2 mm Hg. During this distillation diminishing of linoleic and linolenic acid contens was observed. But the appearence of short chain acids (the chain's length up $C_{14:0}$) was observed. They existed in first running. The loss of erucic acid can be explained by the fact that it is the main constituent of static hold np of distillation column.

Table 4

Composition of waste fatty acids distilled at deaerated steam

Fatty acid	Waste fatty acids	First running	Distillate	Residue	Total fatty acid percentage
$C_{12:0}$	0.2	0.2	—	—	0.2
$C_{14:0}$	2.8	0.8	0.9	—	1.7
$C_{14:1}$	0.4	0.2	0.1	—	0.3
$C_{14:2}$	0.3	0.2	0.1	—	0.3
$C_{16:0}$	30.5	2.6	18.1	4.6	25.3
$C_{16:1}$	3.6	0.3	1.9	0.3	2.5
$C_{16:2}$	0.8	—	0.5	0.1	0.6
$C_{17:0}$	0.4	—	0.3	0.1	0.4
$C_{18:0}$	16.4	1.6	11.0	3.0	15.6
$C_{18:1}$	40.5	0.1	28.7	7.4	36.2
$C_{18:2}$	3.2	—	1.7	—	1.7
$C_{20:0}$	0.3	—	—	—	—
$C_{20:1}$	0.6	—	—	0.4	0.4
$\Sigma C < C_{12:0}$	—	3.0	—	—	3.0

The boiling point of fractions: first running 174—182 °C, distillate 182—197 °C, p = 2 mm Hg.
The amount of crude fatty acids was 600 g.
The quantity of steam used during the distillation was 4.2 g.

In Table 4 there is given the balance of waste fatty acids distillation at dearated steam and a pressure of 2 mm Hg.

In the first running short chain carboxylic acids (chain length up to $C_{12:0}$) were present. They did not exist in crude fatty acids. Analogous balances of fatty acids contents for each distillation were estimated. It was observed that the fatty acids losses were caused mainly by the static hold np of distillation column. But it should be stressed that the diminishing of such unsaturated acids contents as oleic, linoleic, linolenic acid wer caused by polymerization or degradation. The smallest losses — in the case of rapeseed oil and waste fatty acids were observed during processes carried at deaerated steam atmosphere and the greatest losses at the air atmosphere.

Saponification and neutralization values of individual fractions coresponded with acid composition. In residues there were great differences between the saponification and acid values.

The iodine values changes in proportion to the contents of unsaturated fatty acids.

The first running was always characteristic of higher peroxide values than the distillate but lower than the residues. The fractions of distillations carried at nitrogen and deaerated steam were of lower peroxide values than the fractions of distillations carried at air and nondeaerated steam.

The contents of carbonyl compounds, unsaponifiable matters, hydrocarbons and polymers in the fractions were investigated.

Table 5

Contents of unsaponifiable matters in fractions obtained during distillation of waste fatty acids and rapeseed oil fatty acids at air presence

Pressure (mm Hg)	Waste fatty acids			Rapeseed oil fatty acids		
	first running	distillate	residue	first running	distillate	residue
2	2.2	0.8	8.3	1.4	0.9	7.9
4	2.9	1.5	10.1	1.7	1.0	10.3
6	3.5	1.9	14.1	2.1	1.2	14.8

Table 5 shows the contents of unsaponifiable matters in fractions of distillations at air atmosphere.

The greatest amounts of unsaponifiable matters were observed in residues and in the first runnings. It was observed that the higher pressure makes the contents of unsaponifiable matters in all distillation fractions.

By comparing the distillations carried out at the pressure of 2 mm Hg and 6 mm Hg it was found a nearly double growth of unsaponifiable matters contents in the residues. Table 6 gives the percentage contents of unsaponifiable matter in the distillation fractions carried out at deaerated steam atmosphere. In comparison to distillations carried at air atmosphere there is a distinct diminishing of unsaponifiable matters contents appears especially in the first runnings and distillates. Their contents in the residues diminishes too. But increasing of pressure causes analogously as in the latter table growth of unsaponifiable substances contents.

Table 6

Contents of unsaponifiable matters in fractions obtained during distillation of waste fatty acids and rapeseed oil fatty acids at deaerated steam

Pressure (mm Hg)	Waste fatty acids			Rapeseed oil fatty acids		
	first running	distillate	residue	first running	distillate	residue
2	0.6	0.2	4.8	0.4	0.2	4.8
4	0.9	0.4	6.1	0.8	0.3	6.2
6	1.1	0.7	9.1	1.0	0.5	9.0

The hydrocarbons were isolated by column chromatography from the unsaponifiables matters of residues. Their contents in residues are shown in Table 7.

Table 7

Contents of hydrocarbons in residues obtained during distillations of waste fatty acids and rapeseed oil fatty acids

Atmosphere	Waste fatty acids			Rapeseed oil fatty acids		
	pressure (mm Hg)			pressure (mm Hg)		
	2	4	6	2	4	6
Air	3.1	4.2	6.1	4.8	6.6	8.2
Nitrogen	1.0	1.8	3.0	1.9	3.8	5.0
Aerated steam	1.8	2.4	4.6	1.0	1.2	2.8
Deaerated steam	1.0	1.3	2.5	0.9	1.0	2.0

The residues of distillations at air atmosphere contain more of hydrocarbons than those from the distillations carried out at nitrogen, deaerated and nondearated steam atmosphere. Comparing the distillations of waste fatty acids at air pressure 2 mm Hg we observed three times as great growth of hydrocarbons contents in residues as during distillations carried at deaerated steam and nitrogen.

For rapeseed oil fatty acids the growth of hydrocarbons contents during the distillations at air atmosphere is nearly five much as great. But with the progress of pressure in all residues we observe the growth of hydrocarbons contents. Their smallest amounts contain residues of distillations carried at deacrated steam.

Small amount of carbonyl compounds existed in all distillation fractions.

Table 8 gives amounts of those compounds for distillations carried at air atmosphere.

The distillations both of rapeseed oil fatty acids and waste fatty acids contained below 1% of carbonyl compounds, but they were con-

Table 8

Contents of carbonyl compounds in fractions obtained during distillation of waste fatty acids and rapeseed oil fatty acids at air presence

Pressure (mm Hg)	Waste fatty acids			Rapeseed oil fatty acids		
	first running	distillate	residue	first running	distillate	residue
2	0.5	0.2	1.5	0.8	0.2	1.8
4	0.7	0.3	1.8	1.0	0.4	2.4
6	0.9	0.4	2.2	1.5	0.6	3.6

tained mainly in residues. First runnings contained more carbonyl compounds than distillates.

In the fractions of distillations at nitrogen and nondeaerated steam atmosphere, the contents of carbonyl compounds were lower than in the case of distillations carried out at air atmosphere. The lowest contents of carbonyl compounds were established in the distillation at deaerated steam atmosphere. Their contents are shown in Table 9.

Table 9

Contents of carbonyl compounds in fractions obtained during distillation of waste fatty acids and rapeseed oil fatty acids at deaerated steam

Pressure (mm Hg)	Waste fatty acids			Rapeseed oil fatty acids		
	first running	distillate	residue	first running	distillate	residue
2	0.4	0.1	0.1	0.2	0.1	0.9
4	0.5	0.2	1.7	0.3	0.1	1.8
6	0.6	0.2	1.8	0.5	0.2	2.1

Distillates of rapeseed oil fatty acids and waste fatty acids contain small amount of carbonyl compounds. The contents of those compounds in residue did not exceed 2%.

The polymers — which are compounds of great molecular weight occurs in residues only. The contents of those compounds in residues clearly depended on the process conditions. The contents of polymers in the residues are given in Table 10.

Table 10

Contents of polymers in residues obtained during distillations of waste fatty acids and rapeseed oil fatty acids

Atmosphere	Waste fatty acids			Rapeseed oil fatty acids		
	pressure (mm Hg)			pressure (mm Hg)		
	2	4	6	2	4	6
Air	23.1	28.5	34.5	29.3	35.6	49.8
Nitrogen	18.9	23.5	29.5	21.5	27.6	31.6
Aerated steam	20.1	24.8	33.8	20.4	29.3	35.6
Deaerated steam	18.2	22.6	26.9	17.9	20.0	30.0

During the fatty acids distillation at air atmosphere the formation of great amounts of polymers was found. In the case of rapeseed oil fatty acids their higher contents is caused by the presence of larger amount of unsaturated acids which undergo the polymerization. The pressure increase during the distillation causes formation of greater amounts of those compounds. The smallest quantities of polymers are formed, when deareated steam and nitrogen were used.

Also the presence of oxy acids in the distillation fractions was studied. It was stated that they exist in trace amount (0.1%) in residues only.

It results from the presented data, that with the pressure growth during the distillation — at the same atmosphere — an increase took place of accomparying substances concentrated in the residues like: unsaponifiable matters, hydrocarbons, carbonyl compounds and polymers. In the distillation fractions also increase the contents of unsaponifiable matters and carbonyl compounds.

While discussing distillations carried in analogous conditions it was observed that the distillation proceed best at 2 mm Hg. at deareated steam. The air presence caused formation of great amounts of transformation products of fatty acids and other substances existing in raw material. It is obvious that the quantities of compounds formed during the distillation and influence of parameters of the process depend on the composition of raw fatty acids.

REFERENCES

1. **Fedelli F., Camerati F.: Rivista Italiana, 1968, 45, 663.**
2. **Graille J.: Revue Francaise des Corps Gras, 1971, 18, 537.**
3. **Guillaimin R.: Revue Francaise des Corps Gras, 1969, 16, 119.**
4. **Stage H.: Fette Seifen Anstrichmittel, 1973, 75, 160.**
5. **Stage H.: Fette Seifen Anstrichmittel, 1973, 75, 298.**
6. **Stage H.: Fette Seifen Anstrichmittel, 1971, 73, 10.**
7. **Stage H.: Fette Seifen Anstrichmittel, 1971, 73, 10.**
8. **Stage H.: Fette Seifen Anstrichmittel, 1970, 72, 229.**
9. **Stage H.: Fete Seifen Anstrichmittel, 1970, 72, 353.**

W. Zwierzykowski, H. Szeląg, B. Orzęcka, E. Ledóchowska

PRZEMIANY KWASÓW TŁUSZCZOWYCH PODCZAS ICH DESTYLACJI

Streszczenie

Przeprowadzono destylację frakcjonowaną, próżniową kwasów tłuszczowych oleju rzepakowego i kwasów tłuszczowych tłuszczów odpadowych.

Celem określenia przemian kwasów tłuszczowych zachodzących podczas tego procesu, wykonano szereg destylacji przy zmiennych parametrach w atmosferze azotu, powietrza, pary wodnej odpowietrzonej i nieodpowietrzonej. Przemiany śledzono określając skład kwasów tłuszczowych oraz ilościowe zmiany substancji nie-

zmydlających się, węglowodorów, związków karbonylowych, oksykwasów i polimerów. Stwierdzono, że ze wzrostem ciśnienia podczas destylacji z tym samym czynnikiem następuje wzrost zawartości w pozostałościach podestylacyjnych substancji towarzyszących kwasom tłuszczowym, zwłaszcza polimerów.

Biorąc pod uwagę destylacje prowadzone w analogicznych warunkach, zaobserwowano, że najlepiej przebiega destylacja w atmosferze pary wodnej odpowietrzonej, a najgorzej w atmosferze powietrza. Obniżenie ciśnienia poprawia jakość destylatu, a także przedgonu i pozostałości podestylacyjnej.

В. Звежиковски, Г. Шелёнг, Б. Оженцка, Э. Ледуховска

ПРЕОБРАЗОВАНИЯ ЖИРНЫХ КИСЛОТ ВО ВРЕМЯ ИХ ДИСТИЛЛЯЦИИ

Резюме

Проводили фракционированную вакуумную дистилляцию жирных кислот рапсового масла и отбросных жиров.

С целью определения преобразований жирных кислот происходящих в ходе указанного процесса проводили ряд дистилляций при изменчивых параметрах в атмосфере азота, воздуха, водяного пара обезвоздушенного и необезвоздушенного. Преобразования наблюдались при определении состава жирных кислот и количественных изменений неомывающихся веществ, углеводов, карбоксильных соединений, оксикислот и полимеров. Установлено, что по мере роста давления во время дистилляции с одним и тем же фактором происходит повышение содержания в последистилляционных остатках веществ сопутствующих жирные кислоты, особенно полимеров.

В случае дистилляций проводимых в аналогичных условиях установлено, что лучше всего дистилляция проходит в атмосфере обезвоздушенного водяного пара, а хужевсего — в атмосфере воздуха. Снижение давления улучшает качество дистиллята, а также первого прогона и последистилляционного остатка.