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Interesterification reaction activity, fatty acid composition and selectivity ratio of soybean oil

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RESUMEN

Relación entre la actividad de la reacción de interesterificación, la composición en ácidos grasos y la selectividad en aceite de soja.

Se han llevado a cabo reacciones de interesterificación mediante la adición de ácido oleico a aceite de soja en la relación 1:2 w/w bajo diferentes condiciones de temperatura, agitación y porcentaje de catalizador.

La evaluación de la interesterificación de los aceites se realizó por determinación del índice de saponificación, el índice de iodo y la composición en ácidos grasos. Este estudio mostró que el ácido linolenico, que es responsable de la inestabilidad del flavor del aceite de soja y considerado como factor primario que contribuye a la deterioración de este aceite, podría ser reducido a cantidades menores o iguales al 3%.

PALABRAS-CLAVE: Aceite de soja — Acido graso (composición en) — Acido oleico — Indice de iodo — Indice de saponificación — Interesterificación — Niquel.

SUMMARY

Interesterification reaction activity, fatty acid composition and selectivity ratio of soybean oil.

The interesterification reaction was carried out by adding oleic acid to soybean oil by ratio 1:2 w/w under different conditions of temperature, stirring and catalyst percentages.

Assessment of the interesterification of oils was reported by determination of saponification value, iodine value and fatty acids composition. This study showed that linolenic acid which is responsible for flavour instability of soybean oil and consider as primary factor contributing to deterioration of this oil could be reduced to less than or equals 3%.

KEY-WORDS: Fatty acid (composition) — Interesterification — Iodine value — Nickel — Oleic acid — Saponification value — Soybean oil.

1. INTRODUCTION

Interesterification of edible oils is an important process for the modification of physical and functional properties as are hydrogenation and fractionation (1). It is usually involves at least two oils that have different fatty acids composition (2). The classical interesterification is characterized by a randomization in the distribution of acyl moities in the triacylglycerol molecules by applying a chemical catalyst such as sodium alkoxide, sodium potassium alloy, metalic sodium and sodium hydroxide (3, 4). Interesterification is an old process whereby fats and olis can be randomized to improve plasticity, crystal habit or functional properties (5).

Chemical interesterification causes a statistical randomization of fatty acid distribution that leads to modification in triacylglycerols composition and, consequently, in physical behavior (6).

The increase in stability was attributed to a decrease in the amount of linolenic acid in soybean oil (7). The lack of frying stability and the poor frying oil performance of soybean and canola oils have been well documented (8, 9). Linolenic acid has been identified by various researchers as the primary factor contributing to deterioration of these oils during high-temperature use (10).

2. MATERIALS AND METHODS

Soybean oil and oleic acid were obtained from Cairo Company of Fats and Soap. The interesterification reaction carried out by adding oleic acid to soybean oil with ratio 1:2 w/w and 0.2% Nickel catalyst at 60°C with stirring for 2 hours in oil bath. The experiment was repeated for 4 and 6 hours respectively, under the same conditions of temperature and catalyst percentage. The experiment was re-done at temperatures of 90 and 120°C under same conditions of catalyst percentage, temperature and stirring times reported before. The experiment giving the optimum results was repeated with 0.4% and 0.6% Nickel catalyst at 90°C with stirring for 4 hours.

The saponification value (S.V) and iodine value (I.V) of interesterified oil were determined by method described in AOCS (11, 12).

Analysis of fatty acids was done by gas liquid chromatography (13) using Varian 3700 and flame ionization detector where the conditions are:

— Column package 20 % diethylene glycol succinate (DEGS) on chromosorb W (60 - 80 mesh) column length 6 feet with internal diameter of 0.25 inch.

— Column temperature for fatty acids is isothermal at 195°C. Injection temperature is 220°C but detector temperature is 300°C.

— Carrier gas (He) flow rate is 30ml/min and hydrogen flow rate is 30ml/min also, but air flow rate is 300ml/min.

3. RESULTS AND DISCUSSION

Concerning this study, the chemical characteristics of interesterified soy oil such as iodine and saponification values are registered in tables I and II. Table I shows the results of chemical characteristics of interesterification process at 60, 90 and 120°C for 2, 4 and 6 hours of stirring using 0.2% Nickel catalyst. On the other hand table II reports the chemical characteristics of soy oil which was interesterified at 90°C for 4 hours of stirring using 0.4 and 0.6 % Nickel catalyst. Since iodine value reached a low comparable with that of soy oil before carring out interesterification process (control) while saponification values moved just a little after interesterification.

Table I

Chemical characteristic of interesterified soy oil at different temperature and time of stirring using 0.2% Nickel catalyst.

Heating temp.	2 hours stirring		4 hours stirring		6 hours stirring	
	I.V.	S.V.	I.V.	S.V.	I.V.	S.V.
60°C	117.1	194.8	117.8	195.5	117.3	200.3
90°C	110.3	195.6	110.7	196.8	114.1	202.5
120°C	110.3	196.8	109.5	202.6	110.1	202.9

* Iodine value of soybean oil (control) was 125.8
** Saponification value of soybean oil (control) was 196.8.

Table II

Chemical characteristic of interesterified soy oil at 90°C and 4 hours stirring using 0.4 and 0.6 Nickel catalyst

% of catalyst	I.V.	S.V.
0.4%	112.0	207.2
0.6%	115.3	202.5

The iodine number represents true unsaturation of fats and fatty acids only when the double bonds are unconjugated and the structure is not severely hindered, i.e during interesterification process some of the double bonds going to be broken and iodine value moves to a low level. An interesterification at 90°C for two hours using 0.2% of nickel catalyst was markedly more active where activity of interesterification process equals droping in iodine value/time. Interesterification reaction using 0.2 % of nickel catalyst at the other temperatures and times of stirring had activity in the range of 1.43 - 4.08 table III whereas the activity of interesterification process using 0.4 and 0.6 % of nickel catalyst at 90°C for 4 hours stirring were 3.45 and 2.57 respectively. We may trace that iodine values of the interesterified soy oil met linoleic and linolenic acid percentages. Also decreasing or increasing percentages of fatty acids are proportional to their molecular weights and the total molecular weights of individual fatty acids related to saponification value of the oil.

Table III

Activity of interesterification reaction by using 0.2% Nickel

Heating	2 hours		4 hours		6 hours	
	ΔI.V.	ΔI.V./time	ΔI.V.	ΔI.V./time	ΔI.V.	ΔI.V./time
0		—	—	—	—	—
60°C	8.7	4.35	8.0	2.0	8.5	1.42
90°C	14.7	7.35	15.1	3.78	11.7	1.95
120°C	14.7	7.35	16.3	4.07	15.7	2.62

Where IV = Droping in iodine value
IV/time = Activity of interesterification process.

Tables IV-VII shows fatty acids composition of soy oil after doing interesterification process at different temperature and several times of stirring using various percentages of nickel catalyst comparable with that of soy oil before interesterification process. The results appear decreasing of linoleic and linolenic acids while increasing of oleic and stearic acids percentages.

From the changes in fatty acids composition during interesterification, the selectivity ratio (SR) was calculated using Allen's method (14) as original proposed by Albright (15).

[SR is defined as K_2/K_3, where $K_2 = 1-L_o$, $K_3 = S-S_o$ (L_o and S_o) represent the linoleic and stearic acid contents in the original oil (control) and L and S in the interesterified sample (table VIII). In the same manner the selectivity ratio (SR) regarding linolenic acid would be calculated and recorded in table IX. The highest values of selectivity ratio of interesterification reaction are 0.08 and 0.04 for linoleic and linolenic acid concerning the reaction using 0.2 % nickel catalyst at 60°C for 2 hours of stirring. The selectivity ratio during interesterification reaction using 0.4 and 0.6 % of nickel catalyst at 90°C for 4 hours stirring were 0.03 and 0.03 respectively for linoleic acid and 0.03 and 0.02 respectively for linolenic acid.

Table IV
Fatty acid composition of interesterified soy oil at 60°C using 0.2 % Nickel catalyst

Fatty acid	control	2 hours stirring	4 hours stirring	6 hours stirring
$C_{16:0}$	15.0	9.62	10.02	9.60
$C_{18:0}$	9.2	12.89	18.13	26.20
$C_{18:1}$	20.8	36.77	31.29	24.30
$C_{18:2}$	48.4	34.53	33.52	33.0
$C_{18:3}$	7.2	6.20	6.98	6.60

Table V
Fatty acid composition of interesterified soy oil at 90°C using 0.2 % Nickel catalyst

Fatty acid	control	2 hours stirring	4 hours stirring	6 hours stirring
$C_{16:0}$	15.0	9.52	9.73	10.22
$C_{18:0}$	9.2	18.13	12.96	29.75
$C_{18:1}$	20.8	28.30	35.66	22.16
$C_{18:2}$	48.4	37.58	35.76	30.97
$C_{18:3}$	7.2	6.48	5.87	6.88

Table VI
Fatty acid composition of interesterified soy oil at 120°C using 0.2 % Nickel catalyst

Fatty acid	control	2 hours stirring	4 hours stirring	6 hours stirring
$C_{16:0}$	15.0	10.24	9.72	10.10
$C_{18:0}$	9.2	18.86	16.68	26.72
$C_{18:1}$	20.8	31.54	31.89	25.30
$C_{18:2}$	48.4	33.27	35.15	31.20
$C_{18:3}$	7.2	6.10	6.50	6.60

Table VII
Fatty acid composition of interesterified soy oil at 90°C and 4 hours stirring using 0.4 and 0.6 % Nickel catalyst

Fatty acid	control	0.4 % Ni	0.6 % Ni
$C_{16:0}$	15.0	10.70	12.0
$C_{18:0}$	9.2	38.40	39.60
$C_{18:1}$	20.8	43.30	39.20
$C_{18:2}$	48.4	6.11	5.30
$C_{18:3}$	7.2	1.11	3.90

Table VIII
Selectivity ratio of linoleic acid during interesterification reaction using 0.2 % nickel catalyst.

Time of stirring	60°C			90°C			120°C		
	$S-S_o$	L/L_o	Selectivity ratio	$S-S_o$	L/L_o	Selectivity ratio	$S-S_o$	L/L_o	Selectivity ratio
2	3.69	0.71	0.08	8.93	0.77	0.03	9.66	0.68	0.033
4	8.93	0.69	0.03	3.76	0.74	0.07	7.48	0.72	0.037
6	17.0	0.68	0.018	20.55	0.64	0.017	17.52	0.64	0.02

Table IX
Selectivity ratio of linolenic acid during interesterification reaction using 0.2 % nickel catalyst.

Time of stirring	60°C			90°C			120°C		
	$S-S_o$	Ln/L_o	Selectivity ratio	$S-S_o$	Ln/L_o	Selectivity ratio	$S-S_o$	Ln/L_o	Selectivity ratio
2	3.69	0.861	0.04	8.93	0.9	0.011	9.66	0.85	0.02
4	8.93	0.96	0.004	3.76	0.82	0.05	7.48	0.90	0.013
6	17.0	0.92	0.005	20.55	0.96	0.001	17.52	0.92	0.005

Figures 1-5 show some relations of data derived from the results of this study.

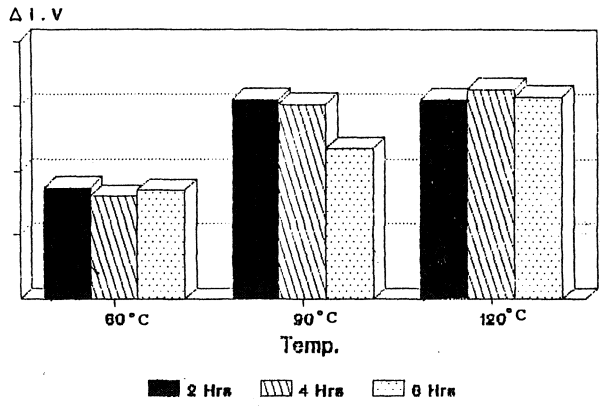

Figure 1
Relation between temperature and dropping in iodine value for 2, 4 and 6 hrs using 0.2 % nickel catalyst

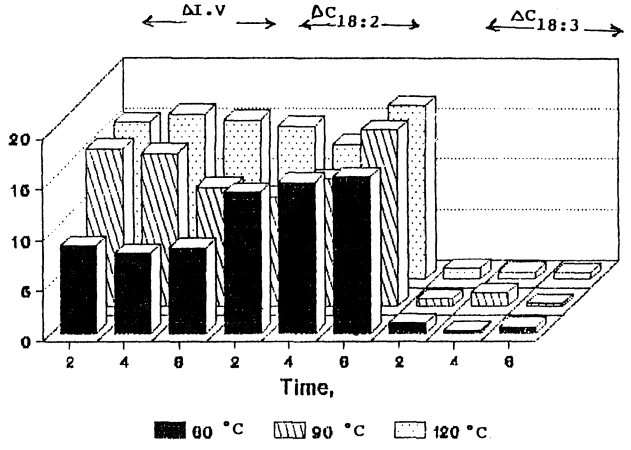

Figure 2
Relation between dropping in iodine value and dropping in linoleic and linolenic acids using 0.2 % nickel catalyst

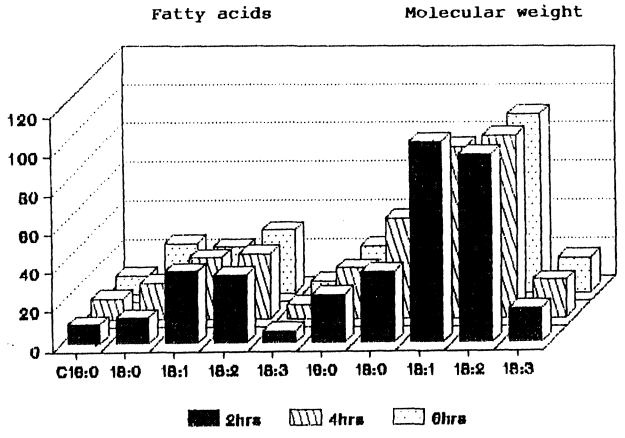

Figure 3
Relation between fatty acid percentages and their corresponding molecular weights for interesterified at 60°C using 0.2 % nickel catalyst

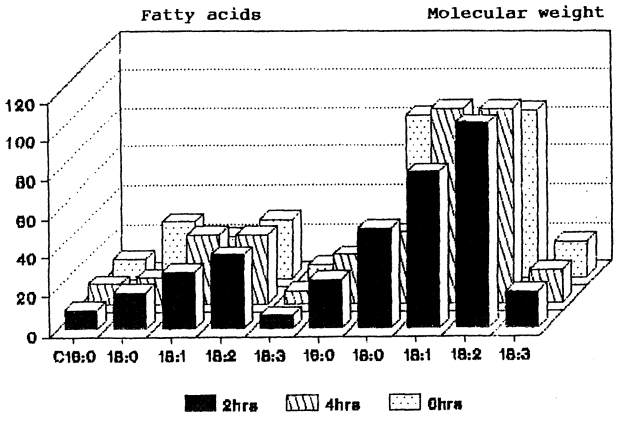

Figure 4
Relation between fatty acid percentages and their corresponding molecular weights for interesterified soybean oil at 90°C using 0.2 % nickel catalyst

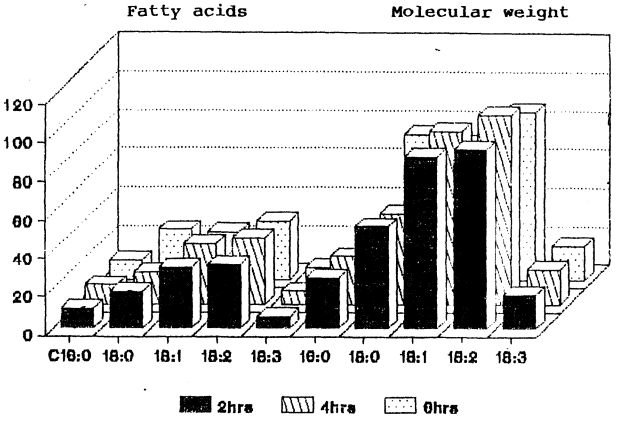

Figure 5
Relation between fatty acid percentages and their corresponding molecular weights for interesterified soybean oil at 120°C using 0.2 % nickel catalyst

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