

EFFECT OF PROCESS CONDITIONS ON PHYSICAL AND CHEMICAL PROPERTIES OF HYDROGENATED FATS: MONITORING OF COTTONSEED OIL HYDROGENATION PROCESS

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Abstract

Hydrogenation process is simply defined as the addition of hydrogen molecules to double bonds of triglycerides. Although the definition is stated simply, mechanism of reaction involves complex mass transfer steps resulting in considerable effects on various physical and chemical characteristics of final product. In this study, changes in fatty acid composition, geometrical and positional isomer content, melting point and solid fat content were used as tools for monitoring cottonseed oil hydrogenation. Results were evaluated numerically by calculating reaction rate and linoleic selectivity. Reactions were carried out at three process temperatures and the effects of temperature on miscellaneous properties of the fat were discussed. Results showed that hydrogenation tends to produce higher saturate towards the end of the reaction especially under low selectivity conditions resulting from lower reaction temperature. This is accompanied by lower rates of trans isomer formation with higher saturates. Fats, solid fraction of which is mostly comprised of trans isomers, differ considerably from those having higher amounts of saturates, in physical characteristics such as melting point and solid fat content, indicating that the processor should monitor the reaction in order to identify the level where desired properties are achieved.

Key words: cottonseed oil, hydrogenation, trans isomerization, selectivity, solid fat content, melting point

HİDROJENE YAĞLARIN FİZİKSEL VE KİMYASAL ÖZELLİKLERİNE İŞLEM KOŞULLARININ ETKİSİ: PAMUK YAĞININ HİDROJENASYON SÜRECİNİN İNCELENMESİ

Özet

Hidrojenasyon işlemi; yağ içerisinde çözünmüş bulunan hidrojen moleküllerinin doymamış çift bağlara eklenmesi olarak tanımlanmaktadır. Reaksiyon, tanım olarak basit bir eklemlemeyi ifade etmekle birlikte; son ürünün fiziksel ve kimyasal özellikleri üzerinde oldukça önemli etkileri olan kütle transfer kademelerini içeren karmaşık bir mekanizmaya sahiptir. Bu çalışmada, hidrojenasyon süreci; yağ asidi kompozisyonu, geometrik ve pozisyonel izomer içerikleri, erime noktası ve katı yağ içeriği değerlerindeki değişikliklerin belirlenmesiyle izlenmiştir. Analiz sonuçları, hidrojenasyon hızı ve linoleik seçiciliği değerlerinin hesaplanmasıyla sayısal olarak değerlendirilmiştir. Hidrojenasyon reaksiyonu üç farklı sıcaklıkta (130, 150 ve 170 °C) gerçekleştirilerek; işlem sıcaklığının yağın özellikleri üzerindeki etkisi belirlenmiştir. Özellikle düşük reaksiyon sıcaklıklarında; azalan seçiciliğe bağlı olarak doymuş yağ asidi miktarının arttığı görülmüştür. Bu durumun, ürünlerdeki trans izomer miktarında azalmaya da neden olduğu gözlenmiştir. Katı ve yüksek erime noktalı fraksiyonun önemli bir kısmını trans izomer içeren trigliseritlerin oluşturduğu hidrojene yağların; söz konusu fraksiyonu ağırlıklı olarak doymuş trigliseritlerden oluşan ürünlerden erime noktası ve katı yağ içeriği gibi fiziksel özellikler açısından oldukça farklı olduğu bulgulanmıştır. Bu durum; hidrojenasyon süresinin; üründe istenilen fiziksel özelliklere ulaşıldığı noktanın izlenmesi yoluyla belirlenmesi gerekliliğini açığa çıkarmaktadır.

Anahtar sözcükler: pamuk çekirdeği yağı, hidrojenasyon, trans izomerizasyon, seçicilik, katı yağ içeriği, erime noktası

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INTRODUCTION

Oils and fats are subjected to a series of processes to increase their area of use by altering their fatty acid and/or triglyceride compositions. The physical and chemical properties of the starting oil change considerably at the end of such processes. These processes are called fat modification techniques. In the oil industry, three modification techniques are commonly used: hydrogenation, interesterification, and fractional crystallization (1).

Hydrogenation is the oldest and most widely used process in the oil industry. It has been in use since 1900's for various fat modification purposes (2, 3). Hydrogenation can simply be defined as the addition of a hydrogen molecule to the double bonds of triglycerides (4). The oil (liquid) and hydrogen bubbles (gas) meet on the surface of the catalyst particle (solid) during a heterogeneous catalytic process. Nickel particles supported on various porous materials are used as catalysts in hydrogenation of fats and oils. Hydrogenation involves various mass transfer steps. Hydrogen bubbles firstly dissolve in the oil by overcoming the gas-liquid film surrounding each bubble. Then the two reactants; namely, hydrogen and unsaturated triglyceride transfer to the catalyst surface where they are adsorbed. Subsequently, the surface reaction occurs yielding the saturated product, which desorbs from the catalyst surface and diffuses back to the bulk from the catalyst pore (5-7). The course of hydrogenation, and hence the physical and chemical properties of the final product can be considered as a function of the degree that these mass transfer resistances are overcome (8).

The hydrogenation process results in changes in fatty acid composition together with trans isomer content. Depending on the process factors and the composition of starting oil; these changes determine the physical properties of hydrogenated fat. As hydrogenation proceeds, amount of saturates increase together with formation of positional and geometrical isomers (9).

Trans isomers that are formed as a result of partial hydrogenation of oils are of crucial importance from many aspects. The presence of trans fatty acids in fats is criticized to have potential adverse health effects (10). However, a controversy has arisen about this criticism (11). This controversy resulted in several studies aiming to describe processes for minimizing trans isomer formation in

relation with the process factors (12-15). On the other hand, several studies promote formation of trans isomers to achieve various melting characteristics, which are not attainable by increasing the amount of saturates (16).

Melting characteristics of a fat mainly depends on the composition of its solid fractions and is determined by melting point and solid fat content analysis. Solid fractions in a hydrogenated fat are generally mixtures of saturated fatty acids and trans isomers. Trans isomers have melting ranges higher than their respective cis isomers but lower than saturates. Therefore, amount of saturates and trans isomers exerts their effect strongly on melting characteristics of hydrogenated fats (17). Composition of solid fractions is variable and changes as the reaction proceeds. Depending on the melting characteristics that are desired by the processor, the point at which the reaction is to be stopped should be evaluated by monitoring these changes in fatty acid composition and isomerization.

Reaction rate and selectivity rate are stated as parameters affecting several physical and chemical characteristics of hydrogenated fats. Therefore; numerical evaluations; namely selectivity and reaction rate calculations; are also involved while discussing effects of hydrogenation. Several calculation models are proposed for the determination of kinetic rate constants of individual fatty acids; and hence selectivity rates (18-23).

In this study, changes in fatty acid composition, geometrical and positional isomer content, melting point and solid fat content were used as tools for monitoring cottonseed oil hydrogenation. Results were evaluated numerically by calculating the reaction rate and linoleic selectivity. Reactions were carried out at three process temperatures and the effects of temperature on miscellaneous properties of the fat were discussed.

MATERIALS AND METHODS

Refined cottonseed oil having the properties illustrated in Table 1 is used as material during hydrogenation runs. Catalyst used is KE-NF 20 type commercial catalyst (22% Ni) and kindly donated by Sud-Chemie-Germany. Catalyst is added to the oil at 0.3% (wt/wt) concentration. Hydrogenation runs are performed in a batch dead end type converter having a volume of 10 L. Reactor pressure

was 0.5 bar and agitation speed was kept constant at 400 rpm. Required amount of catalyst is added to 8 L of cottonseed oil under agitation.

Table 1. Some Properties of Refined Cottonseed Oil

Iodine value	112
Fatty acid composition (%)	
Myristic	0.88
Palmitic	23.16
Stearic	2.25
Arachidic	0.26
Behenic	0.13
<i>Total saturated fatty acids</i>	26.68
Palmitoleic	0.55
Oleic-cis	16.87
Monoenoic-trans	0.11
Linoleic-cis	55.49
Linoleic-trans	0.09
Linolenic-cis	0.15
Trienoic-trans	0.06
<i>Total unsaturated fatty acids</i>	73.32

The oil-catalyst mixture is heated to reaction temperature under vacuum. Hydrogenation is accepted to start when hydrogen gas is introduced to the system. Catalyst is filtered out after hydrogenation. Hydrogenation runs are carried out at 120 °C, 150 °C, and 170 °C. Hydrogenation reaction is an exothermic reaction, which causes the reactor temperature to rise. The reactor temperature was held at constant temperature by cooling. Samples are taken at intervals based on hydrogen consumption. Total amount of hydrogen introduced is kept constant in each run and is equivalent to hydrogen pressure of 9 bar. Nine samples are collected during the reaction and each interval is named as "hydrogenation levels". Amount of hydrogen introduced is constant and equal to one ninth of the total amount of hydrogen gas in each level.

Fatty acid composition of the samples is analyzed according to IUPAC Method 2.501 by using Hewlett-Packard 5890 Series II gas chromatography (Hewlett-Packard, CO., Palo Alto, CA, USA) with flame ionization detector (FID) and Hewlett-Packard Chemstation (24). A fused silica capillary column coated with 100% cyanopropyl polysiloxane (CP™Sil 88. 50 m×0.23 mm i.d.) was used with helium as carrier gas. Solid Fat Content (SFC) of the products is analyzed with Bruker Minispec PC 100 Pulsed NMR (Germany) spectrometer at

20 °C, 30 °C, and 35 °C (25). Melting point (MP) of hydrogenated fats is determined according to AOCS Method Cc 1-25 (26).

Iodine value of the samples is calculated by using fatty acid composition data according to AOCS methods Cd 1c-85 (26). Reaction rate is calculated by determining the iodine value drop per unit process time. Linoleic selectivity rate is calculated by using algorithm given by Butterfield and Dutton (21). For this purpose, MS-DOS QBasic Microsoft Co. 1987-1992 program is used.

RESULTS AND DISCUSSION

In this study, results are presented and discussed in two sections. In the first section, the course of hydrogenation is investigated by considering the changes in chemical and physical characteristics of the fat as the reaction proceeds. Secondly, the results are evaluated numerically by calculating reaction rate and selectivity.

Changes in chemical and physical properties

Chemical composition of the starting oil changed considerably as the reaction proceeds. Most obvious changes are found in the fatty acid composition. Moreover; formation of positional and geometrical isomers are also observed during the reaction.

Fatty Acid Composition

Fatty acid composition of the starting liquid oil changed to a large extent during reaction as a result of double bond depletion. Although cottonseed oil is composed of numerous medium-chain fatty acids; total amounts of 18:2, 18:1, and 18:0 is taken into account to facilitate evaluations.

It is easily observed from Table 2 that the most unsaturated fatty acids, which are the dienes are depleted considerably and their total amount decreased to low levels starting from an initial amount of 55.58% and ending at 10.18%, 4.20%, and 3.01%; for runs at 120 °C, 150 °C, and 170 °C; respectively. The effect of reaction temperature is very significant for the depletion of content which is reduced almost to one third by elevating temperature from 120 °C to 170 °C. In case of mono-enes;

a steady increase is observed up to level 7 followed by an almost flat curve indicating that total amount of mono-enes start to remain constant. This is especially apparent in the hydrogenation run at the most elevated temperature (170 °C) resulting from the subsequent faster reduction of mono-enes to saturates after level 7 where diens are about to be depleted at this reaction temperature. As expected; saturates increased exponentially as the reaction proceeds. Highest amount of saturates are formed at the lowest temperature (120 °C).

As a result, fatty acid composition changed to a large extent during hydrogenation although the changes are temperature-dependent. Formation of saturates increases rapidly near the end of each run, indicating that processors should stop the reaction at the point before this incline starts, if major goal is to limit saturates. Moreover, at this stage more rapid conversion of mono-enes to saturate is also evident.

Isomerization

Isomerization of unsaturated fatty acids is an important side reaction exerting considerable effects on the physical properties of final product during hydrogenation. Table 2 shows the changes in geometrical (trans) and positional isomer contents, as double bonds are depleted.

Trans isomer forms of mono-enes comprised almost 70-80% of total geometrical isomers that were formed in cottonseed oil hydrogenation (Table 2). When the related data is examined, it can easily be seen that trans isomer content increased progressively during the reaction at each run. Nevertheless; the rate of this increase can be seen to be falling towards the end of the runs carried out, indicating that the process is close to reaching a peak in trans-fatty acid content. Trans isomerization is found to be temperature-dependent; in other words; elevated reaction temperatures yield in higher rates of trans isomerization.

Table 2. Changes in Chemical Composition of Cottonseed Oil during Hydrogenation

Temperature (°C)	Level	Time (min)	C18:0	C18:1 cis	C18:1 positional	C18:1 trans	C18:1 total	C18:2 total	C18:3 total	Total trans
120	1	9	3.42	16.57	2.77	3.74	23.08	48.28	0.18	5.24
	2	16	3.73	17.92	4.60	5.55	28.04	42.71	0.13	8.50
	3	24	4.91	18.14	5.12	6.19	29.45	40.17	0.12	8.84
	4	32	5.79	18.97	6.51	8.44	33.92	34.18	0.10	12.16
	5	40	7.28	19.82	7.96	11.74	39.52	27.49	0.05	16.44
	6	48	8.66	20.26	9.10	14.13	43.49	22.38	0.05	19.82
	7	57	10.50	20.44	10.03	16.95	47.42	16.43	0.05	22.90
	8	67	12.42	20.44	10.71	16.55	47.70	14.85	0.04	21.83
	9	76	15.00	19.78	10.90	18.67	49.35	10.18	0.05	24.07
150	1	4	3.11	16.04	2.35	2.60	20.99	49.83	0.18	3.33
	2	8	3.50	17.23	3.98	5.90	27.11	42.73	0.14	7.54
	3	13	3.60	18.70	5.62	9.77	34.09	35.34	0.11	12.67
	4	17	4.23	20.14	7.30	13.13	40.57	28.93	0.09	17.04
	5	21	4.34	20.79	8.29	16.23	45.31	23.47	0.05	20.90
	6	25	5.39	21.19	9.44	19.06	49.69	18.59	0.05	24.11
	7	29	6.36	21.83	10.34	22.81	54.98	13.28	0.05	28.11
	8	38	7.35	22.06	10.91	26.20	59.17	7.74	0.05	30.81
	9	42	11.49	19.58	10.41	28.76	58.75	4.20	-	32.13
170	1	2.5	2.81	16.18	2.44	3.36	21.98	49.40	0.18	4.26
	2	5	2.75	17.38	4.15	6.60	28.13	41.87	0.14	8.76
	3	8	3.08	18.93	5.39	10.57	34.89	35.38	0.11	13.66
	4	11	3.15	20.43	6.92	15.62	42.97	27.43	0.06	20.08
	5	13	3.30	21.06	7.74	18.26	47.06	23.01	0.05	23.18
	6	15.5	3.68	22.56	9.38	23.95	55.89	14.34	0.06	29.05
	7	19	4.60	22.94	10.28	28.16	61.38	8.59	0.05	33.31
	8	22	5.85	21.93	10.33	30.04	62.30	5.98	0.04	34.33
	9	27	9.08	17.14	9.86	35.37	62.37	3.01	-	38.11

Positional isomers, which do not significantly affect the physical properties of the hydrogenated fats, are also formed during hydrogenation. Table 2 shows that almost all of the positional isomers are composed of positional isomers of mono-enes. It is obvious that positional isomers are formed as hydrogenation proceeds; although this increase stops near the end of the reaction. Moreover; a decrease; hence conversion to saturates is observed around level 7 and level 8 especially at elevated temperatures.

When isomerization concept is evaluated globally, it should be stated that most of the isomers formed during hydrogenation are trans isomers of mono-enes. Especially at 170 °C, more than half of the total mono-enes are trans isomers. Moreover, although cis and positional isomers started to be converted to stearic acid especially after level 7 in each run; such a decrease is not observed in trans isomerization. Hence, processor should decide the allowed level of trans isomers in the final product to stop the reaction before it reaches to very high concentrations. In this study, melting characteristics are expressed by determining MP and SFC. Results are presented in Table 3.

Melting Point

MP of the final product is obviously a function of fatty acid composition. As discussed above; low hydrogenation temperatures resulted in excessive formation of saturates; yielding a probable increase in trisaturated glycerides. Therefore, highest MP (43.5 °C) is achieved at lowest hydrogenation temperature (120 °C); and visa versa. As shown in Table 2, trans isomer content of products is found to be higher at elevated temperatures. Therefore; less hardened fats with lower MP is achieved by elevated temperature runs yielding in excessive trans isomer formation.

Since total amount of saturates increased progressively towards the end of the reaction; MP of the product is increased drastically after this level. This is mostly apparent at lower temperature runs where saturates reached higher values.

Solid Fat Content

SFC of hydrogenated fats are also determined and presented in Table 3. $SFC_{20^{\circ}C}$, $SFC_{30^{\circ}C}$ and $SFC_{35^{\circ}C}$ values increased as the reaction proceeds for each run. Melting properties expressed in terms of SFC are found to be temperature dependent. When

Table 3. Changes in Physical Properties of Cottonseed Oil during Hydrogenation

Temperature (°C)	Level	Time (min)	Melting point (°C)	SFC (%)		
				20 °C	30 °C	35 °C
120	1	9	21.5	2.42	-	-
	2	16	24.5	2.92	-	-
	3	24	27.5	4.05	0.11	-
	4	32	31.5	7.21	1.89	-
	5	40	32.5	13.27	4.18	1.22
	6	48	37.5	18.92	7.04	3.60
	7	57	40.0	28.08	10.77	4.76
	8	67	41.0	31.62	14.35	6.61
	9	76	43.5	43.25	22.17	13.21
150	1	4	22.0	0.85	-	-
	2	8	26.5	2.35	-	-
	3	13	28.0	7.20	1.06	-
	4	17	31.5	12.22	3.53	-
	5	21	33.0	14.20	3.47	-
	6	25	35.5	27.79	11.99	2.32
	7	29	37.0	29.40	11.61	2.85
	8	38	38.0	38.00	14.87	5.54
	9	42	41.0	53.14	26.47	14.27
170	1	2.5	20.0	1.54	-	-
	2	5	22.5	2.25	-	-
	3	8	27.0	4.76	-	-
	4	11	31.0	10.40	1.05	-
	5	13	33.5	13.54	3.91	-
	6	15.5	34.5	23.72	7.34	0.27
	7	19	36.5	31.26	10.58	2.15
	8	22	37.5	42.05	14.96	6.15
	9	27	40.0	56.55	25.92	11.81

hydrogenation process is carried out at lower temperatures; most of the solid fraction are saturates. Moreover, greater portions of mono-enes are in cis form with limited trans isomer content. On the contrary, elevated temperatures yielded higher ratios of trans isomers which certainly behaves like saturates during melting. Therefore; fats with higher $SFC_{20^{\circ}C}$ are produced at elevated temperature runs whereas; higher $SFC_{35^{\circ}C}$ values are obtained at lower temperature runs. This leads to shallower slopes for SFC curves for fats produced at lower temperatures, whereas these curves show steeper slopes as temperature is raised.

As a result; melting characteristics of the fat, which depends on its area of use, play an important role for hydrogenation processors to decide hydrogenation conditions.

Numerical evaluations

In this study, reaction rate and selectivity are considered as tools for evaluating hydrogenation process.

Reaction Rate

Since the calculation procedures of kinetic rate constants of individual fatty acids is a tedious process and might lead in confusion; an overall hydrogenation rate is taken into account in this study; which is defined as iodine value drop per unit process time. Rate values are calculated for each hydrogenation level with reference to starting liquid oil; and the results are presented in Table 4. It is obvious that elevated temperatures yielded in higher overall hydrogenation rates; that is to say faster hydrogenation runs. It should be pointed out that after a slower start at level 1; overall rate steadily increased at each hydrogenation run. This progressive increase in rate was followed by a decrease towards the end of the reaction possibly due to fast diminishing of the substrate; ie.; unsaturates because of the elevated temperature.

Table 4. Changes in Reaction Rate and Linoleic Selectivity During Hydrogenation

Temperature (°C)	Level	Time (min)	Iodine value	Reaction rate {D(I)/dt}	Linoleic selectivity (SR _{Ln})
120	1	9	108	0.361	2.36
	2	16	103	0.556	3.33
	3	24	99	0.509	2.62
	4	32	93	0.596	2.89
	5	40	85	0.654	3.83
	6	48	80	0.664	4.51
	7	57	72	0.686	5.13
	8	67	70	0.623	4.92
	9	76	63	0.641	5.22
150	1	4	109	0.580	1.19
	2	8	102	1.221	2.17
	3	13	95	1.293	3.83
	4	17	89	1.330	6.49
	5	21	83	1.344	7.68
	6	25	78	1.326	11.27
	7	29	74	1.311	18.13
	8	38	67	1.166	16.01
	9	42	61	1.216	13.02
170	1	2.5	109	0.884	1.95
	2	5	101	2.066	2.54
	3	8	96	2.001	5.29
	4	11	88	2.105	10.38
	5	13	84	2.115	12.24
	6	15.5	76	2.275	23.92
	7	19	71	2.145	33.38
	8	22	67	2.030	25.25
	9	27	62	1.850	20.87

Selectivity

Since cottonseed oil contains trace amounts of trienes; the term “selectivity” refers to Linoleic Selectivity (SR_{Ln}). SR_{Ln} values are calculated by using fatty acid composition data; and results are expressed in Table 4. Higher hydrogenation temperatures led in higher SR_{Ln} values. SR_{Ln} increases from 5.22 to 20.87 when hydrogenation temperature is elevated from 120 °C to 170 °C when final products are considered. This explains the higher formation of saturates at lower hydrogenation temperatures.

CONCLUSION

Hydrogenation; as a widely used fat modification technique; is a complex reaction involving interactions between various process factors. This complexity stands for the major reason for investigating the changes in chemical and physical properties of the fat as hydrogenation proceeds. Results showed that fatty acid composition changed to a large extent yielding in hardening of the fat as the reaction proceeds. Towards the end of hydrogenation; saturates increased progressively resulting a poor SR_{Ln} especially at lower temperatures which indicates the processor should end the process.

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