

Hydrolysis—Hydrogenation of soybean oil and tallow

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ABSTRACT

Hydrolysis reactions are of major importance to the oleochemical industry in the production of fatty acid and their derivatives. Hydrolysis of triglyceride from vegetable oil has been studied under various parameters such as: heterogeneous catalyst, temperature, reaction time and agitation speed. During the hydrolysis of soybean oil and tallow using nickel catalysts on alumina support was verified that the glycerol produced worked as hydrogen donor, allowing the hydrogenation of unsaturated fatty acids produced. Maximum conversion was achieved in 3 hours, catalysts 25% NiO/Al₂O₃, temperature of 250°C and 270°C and 250 rpm.

Keywords: Hydrolysis; Soybean Oil; Tallow; Hydrogenation; Saturated Fatty Acid; Selectivity

1. INTRODUCTION

Vegetable oils are composed by triglycerides. Every triglyceride, or fat, contains three fatty acid chains attached to a single glycerol molecule. These fatty acid chains can be classified as saturated, monounsaturated and polyunsaturated, depending on the type of chemical bonds present. The hydrolysis of triglycerides produces fatty acids and glycerol [1-4]. Saturated fatty acids have high relevance in the food and oleochemical industries.

The glycerol can be used for hydrogen production by catalytic reforming reaction using nickel or platinum catalysts supported on alumina and silica [5].

This paper presents studies and results on producing saturated fatty acid through catalytic hydrolysis of soybean oil and tallow. The catalysts used in the heterogeneous reactions were nickel supported on gamma alumina, synthesized by the method of wet impregnation. The reaction is shown in **Figure 1**.

2. EXPERIMENTAL

2.1. Reactants and Preparation of Catalysts

The raw materials used in this study are soybean oil and tallow. The fatty acid profile of soybean oil and tallow are shown in **Table 1**.

The catalysts used in the heterogeneous reactions were nickel supported on gamma alumina (5% NiO/Al₂O₃, 10% NiO/Al₂O₃ and 25% NiO/Al₂O₃). To prepare the catalyst of nickel supported on alumina was used as metallic precursor a nickel nitrate salt (Ni(NO₃)₂·6H₂O) 97.0% purity). A commercial alumina (100% purity) was used as a catalyst support. In each experiment, 5, 10 and 25% of metal was loaded on alumina using wet impregnation method.

Catalyst Characterization

The synthesized catalysts were characterized by textural analysis techniques, X-ray diffraction (DRX) and X-ray fluorescence spectrometry (XRF).

Samples were analyzed using a commercial XRF instrument. The chemical compositions of Ni/Al₂O₃ catalysts were measured and the results confirmed the certain amount of active metals on catalyst supports (**Table 2**).

Surface areas of catalysts were determined by applying the Brunauer-Emmett-Teller method (BET), for N₂ physisorption at liquid nitrogen temperature (77 K). The pore volume and average pore diameter were calculated applying the Barrett-Joyner-Halenda (BJH) method [6]. **Table 3** shows the results.

This area reduction is possibly due to partial pores blockage of the support by the particles of nickel oxide [7]. The calcined catalysts displayed an isotherm of type IV with H3-type hysteresis.

XRD patterns of the catalysts displays two crystalline phases, one related to γ -alumina with amorphous structure characteristic (JCPDS 49-0063) and the other the bunsenite NiO with cubic structure and space group Fm3m (JCPDS 47-1049). In the case of catalyst 5% NiO

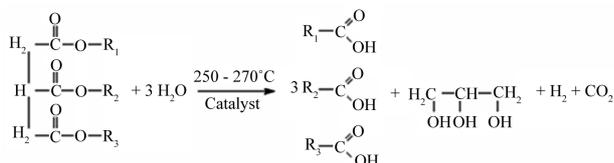


Figure 1. Hydrolysis and hydrogenation of triglycerides.

Table 1. Fatty acid profile of raw materials.

Fatty acid profile	Soybean oil Content % (m/m)	Tallow Content % (m/m)
Myristic (C14:0)	< 0,5	1.0 - 6.0
Palmitic (C16:0)	7.0 - 14.0	20.0 - 37.0
Stearic (C18:0)	1.4 - 5.5	25.0 - 40.0
Oleic (C18:1)	19.0 - 30.0	31.0 - 50.0
Linoleic (C18:2)	44.0 - 62.0	1.0 - 5.0
Linolenic (C18:3)	4.0 - 11.0	-

Table 2. XRF-results of the composition of catalysts.

Catalyst	NiO (%)	Al ₂ O ₃ (%)	Impurities
5% NiO/Al ₂ O ₃	5.33	94.62	0.05
10% NiO/Al ₂ O ₃	11.47	88.47	0.06
25% NiO/Al ₂ O ₃	25.73	73.88	0.09

Table 3. Morphologic characteristic of catalysts obtained.

Catalyst	BET (m ² /g _{cat})	Pore volume (cm ³ /g _{cat})	Average pore diameter (Å)
5% NiO/Al ₂ O ₃	175.38	0.48	85.68
10% NiO/Al ₂ O ₃	164.56	0.44	84.60
25% NiO/Al ₂ O ₃	160.53	0.40	84.06

phase has peaks less visible because it has the least amount of NiO in the catalyst (**Figure 2**).

2.2. Reaction Procedure – Hydrolysis of Soybean Oil and Tallow

Reactions were performed in a stainless steel 300 mL batch reactor (Parr Instruments 4842), maximum pressure of 3000 psi and equipped with a sample withdrawal, stirring, and heating system. Stirring velocity was kept constant (250 rpm). Reaction mixture consisted of 100 g of raw material and 100 g of water, providing a water/raw material molar ratio of 1.

Reagents were introduced together with the appropriated catalyst mass (10% w/w, in relation raw material) and time of reaction (1 and 3 hours) was considered when required temperature (250°C and 270°C) was reached. Products were obtained after 1 and 3 hours of the reaction.

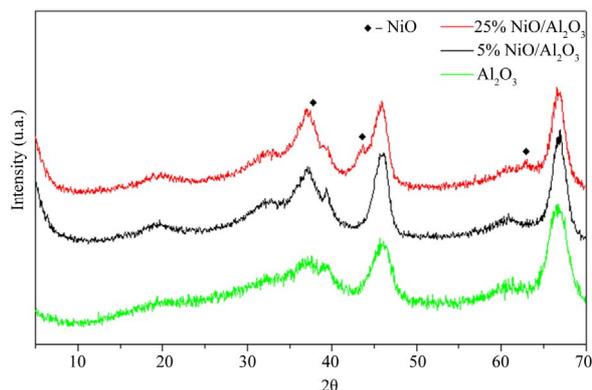


Figure 2. XRD patterns of commercial Al₂O₃, commercial NiO and synthesized NiO/Al₂O₃ catalysts.

2.3. Product Analysis

The goal is to verify the hydrogenation of fatty acids formed, for this, three analyses will be conducted to define the production of fatty acids. These are: Free fatty acid content (FFA), total glycerol and iodine value.

The composition of fatty acid was determined by gas chromatography (ASTM D 6584, EN ISO 14105, EM ISO 14106). It was also determined total glycerol and iodine value. Enzymatic method was used to evaluate total glycerol of samples [8].

3. RESULTS AND DISCUSSION

Hydrolysis results of soybean oil and tallow at 250 and 270°C in one hour of reaction are shown in the **Tables 4**, and in three hours in the **Tables 5**. It is noted in the tables that in one hour of reaction, the values of acidity and iodine are very similar for all experiments (catalyzed and not catalyzed). This effect was observed for both raw materials.

Results obtained in the reactions without catalyst and catalyzed with 5 and 10% nickel oxide, did not change significantly when increasing the reaction time of 1 hour for 3 hours. (**Tables 4** and **5**).

In experiments using 25% NiO/Al₂O₃ were observed changes in fatty acid profiles produced. After 3 hours of reaction, iodine value decreased due to saturation of double bonds (**Tables 5**). The iodine value decreased 47 and 63% for hydrolysis of soybean oil at 250 e 270°C respectively, and 52 and 70% for tallow [9].

The hydrogenation in-situ was confirmed with the gas chromatograph analysis. The chromatogram suggest that occurs preferential hydrogenation of more unsaturated fatty acids. The fatty acid composition of the hydrolysis products of soybean oil are reported in **Figure 3** and for tallow in **Figure 4**.

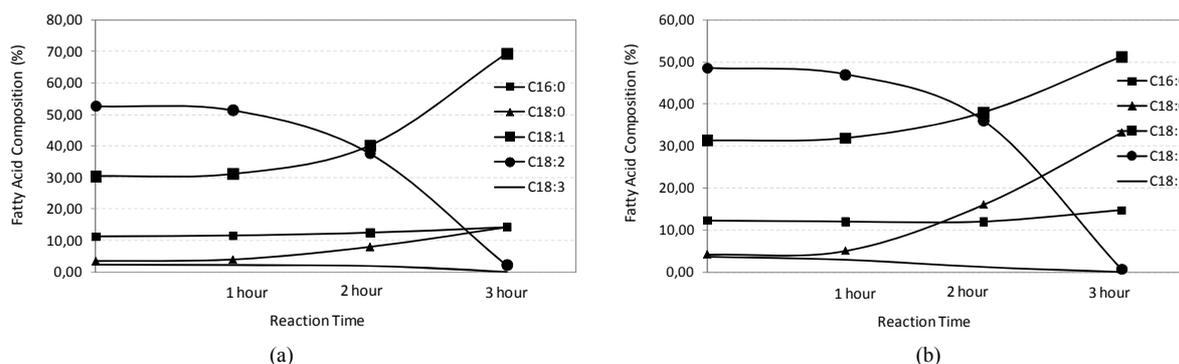
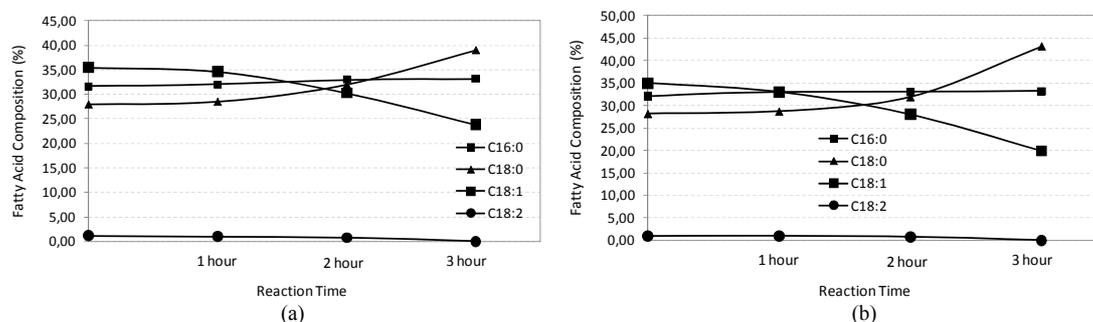
It was observed increase of saturated fatty acids in the hydrolysis of soybean oil, 48 and 66% in reactions at

Table 4. Soybean oil and Tallow hydrolysis (Reaction time: 1h, Catalysts: 5, 10 and 25% of NiO/Al₂O₃).

	5%NiO/Al ₂ O ₃		10%NiO/Al ₂ O ₃		25% NiO/Al ₂ O ₃		Without catalyst	
	250°C	270°C	250°C	270°C	250°C	270°C	250°C	270°C
Soybean oil:								
Glycerol content (%)	2.11	1.24	0.49	0.48	1.36	0.30	1.12	1.01
Acidity (%)	90.57	89.89	89.67	89.89	88.85	87.55	91.25	93.47
Iodine (mgI ₂ /g)	132.22	124.41	130.66	133.01	122.44	139.43	136.82	140.14
Tallow:								
Glycerol content (%)	0,01	0,00	0,52	0,14	0,26	0,32	0,37	0,32
Acidity (%)	85.12	88.53	80.26	87.14	89.16	87.77	84.04	89.05
Iodine (mgI ₂ /g)	46,38	37,98	39,94	32,47	41,81	41,50	46,7	42,08

Table 5. Soybean oil and Tallow hydrolysis (Reaction time: 3h, Catalysts: 5, 10 and 25% of NiO/Al₂O₃).

	5%NiO/Al ₂ O ₃		10%NiO/Al ₂ O ₃		25%NiO/Al ₂ O ₃		Without catalyst	
	250°C	270°C	250°C	270°C	250°C	270°C	250°C	270°C
Soybean oil:								
Glycerol content (%)	2.32	1.04	1.16	1.00	0.43	0.85	1.38	0.89
Acidity (%)	90.04	86.34	82.38	83.35	87.57	85.50	88.67	87.70
Iodine (mgI ₂ /g)	152.25	141.89	139.72	129.91	70.91	47.70	135.24	130.36
Tallow:								
Glycerol content (%)	2.09	1.52	0.60	0.30	0.17	0.15	0.42	0.44
Acidity (%)	85.84	86.34	93.45	85.92	87.55	93.55	87.04	83.72
Iodine (mgI ₂ /g)	41.95	47.48	44.25	35.89	14.64	10.62	30.39	35.59

**Figure 3.** Fatty acid composition of hydrolysis – hydrogenation of soybean oil, using 25% NiO/Al₂O₃, reaction time: 3 h. (a) Temperature: 250°C (b) Temperature: 270°C.**Figure 4.** Fatty acid composition of hydrolysis – hydrogenation of tallow at 250°C, using 25% NiO/Al₂O₃, reaction time: 3 h. (a) Temperature: 250°C (b) Temperature: 270°C.

250 and 270°C, respectively, being 17 and 20% in reactions with tallow.

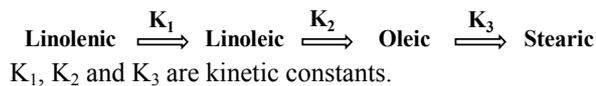
Changes in fatty acid profile is due to the hydrogenation of double bonds of fatty acids produced. The glycerol formed during the hydrolysis of triglycerides in soybean oil and tallow acts as hydrogen donor. The catalytic reforming of glycerol allowed in-situ generation of hydrogen, which is attracted to and reacts rapidly with the double bonds.

During the 3 hours of hydrolysis of soybean oil, using catalyst 25% NiO/Al₂O₃, are hydrogenated linoleic acid and oleic acid [10]. Studies of the kinetics of hydrogenation of these acids show that the rate of hydrogenation of linoleic acid is greater than oleic and stearic [11-13].

Geometry configuration, chemical and physical characteristics of catalyst will determine the selectivity, that is possible observe by selectivity ratio of different fatty acids.

Selectivity Hydrogenation means that hydrogen is

added first to the most unsaturated fatty acids. The high selectivity denotes low level of polyunsaturated fatty acids and high level of monounsaturated. The selectively hydrogenated product is more resistant to oxidation due to the preferential hydrogenation of polyunsaturated acids. In this study, selectivity can be defined as the conversion of the linolenic acid to oleic acid, compared to the conversion of linoleic acid to stearic acid.



It is observed that in the hydrolysis of soybean oil, linoleic acid was completely hydrogenated (more to 95%), this results demonstrates the high selectivity of hydrogenation. Similar result was shown in the reaction with tallow, transforming linoleic acid into oleic acid.

To corroborate quantitatively these results were calculated the selectivities for hydrogenation of linoleic and linolenic acids in the following reactions:

Table 6. SR of linoleic and linolenic acids during hydrolysis – hydrogenation of soybean oil and tallow at 250 and 270°C, using 25% NiO/Al₂O₃.

Temperature: Reaction time (hours):	250°C			270°C		
	1 h	2 h	3 h	1 h	2 h	3 h
Soybean oil:						
Linoleic acid						
Lo	52.63	52.63	52.63	48.52	48.52	48.52
S	4.00	8.00	14.23	5.00	16.00	33.18
So	3.52	3.52	3.52	4.13	4.13	4.13
$K_2 = 1 - Lo$	47.37	47.37	47.37	51.48	51.48	51.48
$K_3 = S - So$	0.48	4.48	10.71	0.88	11.88	29.05
SR = K_2/K_3	98.22	10.57	4.42	58.83	4.33	1.77
Linolenic acid						
Lno	2.28	2.28	2.28	3.75	3.75	3.75
O	31.00	40.00	69.23	31.90	38.00	51.29
Oo	30.29	30.29	30.29	31.30	31.30	31.30
$K_1 = 1 - Lno$	97.72	97.72	97.72	96.25	96.25	96.25
$K_2 = O - Oo$	0.71	9.71	38.93	0.60	6.70	19.98
SR = K_1/K_2	138.59	10.07	2.51	161.49	14.37	4.82
Tallow:						
Linoleic acid						
Lo	1.18	1.18	1.18	0.96	0.96	0.96
S	28.50	32.00	39.01	28.73	31.90	43.12
So	27.95	27.95	27.95	28.18	28.18	28.18
$K_2 = 1 - Lo$	98.82	98.82	98.82	99.04	99.04	99.04
$K_3 = S - So$	0.55	4.05	11.06	0.54	3.72	14.93
SR = K_2/K_3	181.21	24.43	8.94	182.22	26.65	6.63

- Hydrolysis of soybean oil at 250°C and 270°C, using 25% NiO/Al₂O₃ as catalyst, at 1, 2 and 3 hours of reaction time.

- Hydrolysis of tallow at 250°C and 270°C, using 25% NiO/Al₂O₃ as catalyst, at 1, 2 and 3 hours of reaction time.

Linoleic and linolenic acids selectivity was estimated from the selectivity ratio (SR). 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 raw material and L and S in the hydrogenated sample. In the same manner the selectivity ratio (SR) regarding linolenic acid is calculated by: $SR = K_1/K_2$, $K_1 = 1 - L_{no}$, $K_2 = O - O_o$, L_{no} and O_o represent the linolenic and oleic acid contents in the original raw material and L_n and O in the hydrogenated sample. The results for soybean oil and tallow are reported in **Table 6**.

During the hydrogenation of raw materials the selectivity ratios (SR) were high, thus can be assumed that the reactions were selective under these conditions.

The selectivity can be increased with the temperature, or by increasing the pressure and agitation. Analyzing the influence of temperature on SR, it is observed that increasing the temperature of the reaction of soybean oil using catalyst 25% NiO/Al₂O₃ decreases the selectivity of linoleic acid and increases the selectivity of linolenic acid. In comparison, the temperature has not significant influence on the reaction with tallow.

Results of high selectivity in hydrogenation of linoleic acid and linolenic acid were observed only in reactions catalyzed by 25% NiO/Al₂O₃, it is known that commercially employed Ni catalyst has a limited linoleic selectivity [15].

4. CONCLUSIONS

The hydrolysis of soybean oil and tallow were studied in this paper. Hydrogenation occurs in-situ during the hydrolysis, producing large amount of saturated and mono unsaturated fatty acids, such as stearic and oleic acids. These effects were best manifested under 3 hours of the reaction and with the catalysts 25% NiO/Al₂O₃.

The glycerol formed during the hydrolysis behaves as a hydrogen donor. The reform of the glycerol generates the in-situ hydrogen, hydrogenating the fatty acids produced. High hydrogenation selectivity of linoleic and linolenic acid were observed in the reactions using 25% NiO/Al₂O₃. It was not observed hydrogenation of unsaturated fatty acids during the hydrolysis using 5 and

10% NiO/Al₂O₃.

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