Effect of Catalyst Preparation on the Selective Hydrogenation of Vegetable Oil Over Low Percentage Pd/Diatomite Catalysts

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Abstract

Hydrogenated vegetable oils contain high contents of *trans*-fatty acids. Because of the increased health concern about *trans*-fatty acids, new hydrogenations have been studied to seek ways for substantial reduction of the *trans*-fatty acids in the hydrogenated products. In this research, activated diatomite has distinctive properties as a support for hydrogenation catalysts. Investigation of textural properties of raw and purified diatomite samples reveals that during acid activation surface area increases significantly. Although, acid activation of diatomite is a commonly chemical modification to enhance its adsorption capacity. We are preparing adsorption method to synthesize low percentage 0.2% of Pd/Diatomite catalyst. The activated diatomite and the obtained catalyst was characterized by using thermogravimetric analysis (TGA), Brunauer-Emmett-Teller surface area analysis (BET), scanning electron microscopy (SEM-EDAX), transmission electron microscopy (TEM). It was utilized for hydrogenation of sunflower oil using the Parr reactor in laboratory testing a variety of temperature (70, 90, 110 ºC) and canola oil in industrial testing, at temperature 90 ºC and 0.5 MPa pressure and compared to commercial nickel catalyst (Pricat-9910) at 150 ºC, 0.5 MPa pressure agitation of 800 rpm for 160 min. The changes in iodine value, fatty acid composition, *trans*-fatty acids, melting point and solid fat content were investigated on partial hydrogenated sunflower oil and canola oil. The experimentally obtained results show that the palladium catalyst is the most active compared to the commercial catalyst. Lower hydrogenation temperature used 0.2% Pd/Diatomite catalyst, significant reducing the formation of *trans*-content by 13% in fat.

Introduction

The hydrogenation of vegetable oils is a very important practice in the modifications of fats and oils. Hydrogenated products are starting materials used in the food, pharmaceutical and chemical industries [1-3]. During hydrogenation of oils into margarine, shortenings, or partially hydrogenated oil, mainly trans-fatty acids (TFA) are formed due to cis/trans isomerization. Health authorities worldwide have shown that trans-isomer negative effects for human health. High intake of TFA has been associated with increased risk of coronary heart disease, diabetes mellitus and decrease HDL-cholesterol and promotes inflammation [4-5].

The World Health Organization recommended in 2003 that *trans* fats be limited to less than 1% of overall energy intake [6]. Nowadays, Ni-catalysts are most commonly used for vegetable oils hydrogenation in industrial hydrogenation its carry out at temperatures between 150 and 220 ºC and pressure ranging from 10-60 psig, this conditions of hydrogenation using Ni catalysts promote the formation of *trans*-isomers and products of thermal decomposition of fatty acids, as a consequence, soluble nickel by leaching found in hydrogenated oils can react with the triglycerides to form fat-soluble salts, its salts may lead to the cause product toxicity [7-9].

So, catalytic hydrogenation of vegetable oil has seen a lot of advances recent years, especially regarding efforts to reduce the TFA. Researchers have investigated the use of mainly different noble metal

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catalysts (such as Pd, Pt and Ru), to improve selectivity and activity of the hydrogenation process [10-12]. Ecological friendly palladium catalysts are the most active in the wide range of temperature and hydrogen pressure, however, more expensive. Palladium (Pd) catalysts have been reported to be effective in hydrogenation due to their low toxicity, ability to work under moderate conditions and also because their performance can be altered by combination with other materials [13], reported that [14-15], palladium particles supported on various porous materials are used as catalysts in hydrogenation of fats and oils.

For hydrogenation vegetable oils reaction many researches shows that nickel catalysts are not very active below 130 ºC. Palladium catalysts are active at low temperature of 70 ºC and decreased *trans*-fatty acids in hydrogenation of vegetable oils. Therefore, the main challenge in developing new technologies obtain pure product is to the replacing the nickel catalyst with palladium catalyst can be more efficient and real prospects [16].

In this research work new low content palladium catalysts supported on diatomite were synthesized, investigated for good support qualities, and tested for their hydrogenation activity on vegetable oil in laboratory and experimental-industry testing. The results are compared to those obtained over a commercial nickel catalyst (Pricat-9910).

Experimental

Materials

In this study, we choose a catalyst support using diatomite. The raw diatomite obtained from Aktyubinsk/Kazakhstan and chemical treatment was performed with hydrochloric acid. The refined sunflower oil was obtained from LTD "Maslo-Del" (Almaty city), a commercial Nickel based catalyst (Pricat-9910) was purchased from Johnson Matthey Co (Germany).

Activation of raw diatomite and catalyst preparation

Natural diatomite (D) thermally treated at 500 ºC using a muffle furnace (D-500), then, chemical treated by 0.2N HCl solutions, the suspension were centrifuged, solid (D-500-HCl) was washed by distilled water until the pH = 7 and dried in drying oven 110 ºC for 6 h, finally, acid activated diatomite milled by a ball machine finely. Then, palladium chloride (0.2 wt.% Pd) supported on diatomite (0.2% Pd/D) was prepared by the adsorption method; obtained catalyst was stored in a desiccators after reduction

at 100 ºC under 50 ml/min of H_2. The catalytic performances of the prepared and commercial catalysts were compared.

Support and catalyst characterizations

The surface areas, total pore volume, pore size distribution of the obtained support and catalyst was detected in liquid N_2 by the Brunauer-Emmett-Teller (BET) using a volumetric adsorption analyzer (Model Autosorb-1, Quantachrome Instruments) and by transmission electron microscope (TEM) (JEM-3010). Thermogravimetric analyses (TGA) of samples were performed on a PerkinElmer Pyris Diamond SII thermal analyzer (high-purity N_2, 20 ºC/min). The morphologies of the samples were examined using a scanning electron microscopy "Quanta 3D 200i Dual system, FEI", which also gives the elemental composition of samples (EDAX). Average particle size and particle size distribution was determined using a Malvern Laser particle size analyzer Model No. 2000 Analyzer.

Catalytic hydrogenation of vegetable oil

Hydrogenation of sunflower oil was carried out in a Parr Reactor Model 4848 (Parr Instrument Co., Moline, IL, USA) at various temperature (70, 90, 110, 130 ºC) under 5 atm hydrogen pressure and 600 rpm of agitation speed, using 0.060 g catalyst per 60 ml oil were loaded into the reactor. Prior to the experiment, The reactor was purged with hydrogen gas three times. Pilot testing hydrogenation process carried out in 10 t of capacity batch reactor at 90 ºC and pressure of hydrogen 0.5 MPa by using 0.2% Pd/D catalyst and compared to commercial nickel catalyst (Pricat-9910) at 150 ºC and 0.5 MPa. The oil samples taken regularly were filtered to remove catalyst, analyzed for its iodine value (IV) according to ISO 3961 method [17]. The iodine value of an oil and fat is a measure of unsaturation and was controlled to hydrogenation processes. Analysis fatty acid composition of the hydrogenated oils was determined by capillary gas chromatograph (Chrompack 9001) using the ISO 52677 method [18]. A fused silica capillary column coated with 100% cyanopropyl polysiloxane (CP™Sil88, dimensions 100 m, int: 0.25 mm, 0.20 µm film). Oven temperature was 110 ºC – 5 min, 110-215 ºC (5 ºC/min), 215 ºC – 60 min; detector temperature: 280 ºC; injector temperature: 250 ºC; carrier gas: helium; split ratio 1:50; injection volume: 1.0 µL. Qualitative composition was determined by comparing peak retention times with the respective standards for fatty acids. Melting point was determined using a open capillary tube, to ISO

52179-2003 standard method [19], Solid fat content (SFC) determined using nuclear magnetic resonance (NMR) spectrometry, taking readings from samples in at temperature 10, 20, 30 and 40 ºC [20].

Results and Discussion

Support and catalyst characterizations

Catalyst supports are significant components of a catalyst. The use of a support material allows the active component of the catalyst to have a larger exposed surface area. This is mainly because the hydrogenation reaction takes place at the metal surface. In this work used a catalyst support is natural diatomite, it is a loose, earthy or loosely cemented porous rock of sedimentary origin [21], specific properties: porous structure, high silica content, low density, etc. raw diatomite is not suitable for direct mechanical treatment due to its high humidity level and the smaller diatomite fractions. So, raw diatomite was thermal and chemical treated before synthesis of a Pd catalyst. The thermogravimetric analyses (DTA/TGA/TGD) of the raw diatomite are shown in Fig. 1.
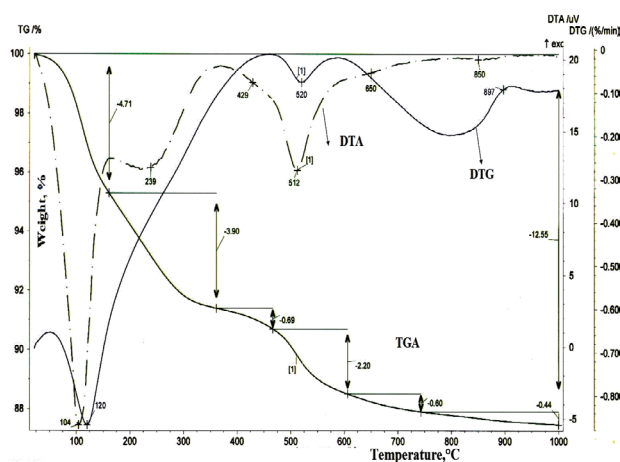

Fig. 1. Thermogravimetric (DTA/TGA/TGD) curves of the raw diatomite.

The DTA curve showed three endothermic effects at 120, 230 and 512 ºC accompanied the weight loss of TGA curve. The main of weight loss occurs at temperatures of 80-120 ºC and 430-650 ºC. At low temperatures, approximately 100 ºC, weight of loss due to evaporation of moisture, carbon compounds and organic impurities combustion starts at about 410 ºC and ends at 650 ºC. Further, there is smoothly reduced weight of the sample up to 1000 ºC. Overall of the weight loss 20-1000 ºC ranges are more than

12 wt.%. Apparently, at the first stage calcination temperature increase to 500 ºC, the fine pores are formed by complete combustion of the organic compounds that are sintered while further heating sintered to form larger pores. That is why, the diatomite sample was optimum calcined temperature at 500 ºC during the support.

The elemental analysis of natural raw diatomite and acid activated forms carried out energy dispersive X-ray spectroscopy (EDXA) expressed as weight of percentages of metal oxides are presented Fig. 2 and Table 1.

As shown in Table 1, the main components of the natural raw diatomite are oxides of: Si, Al and Fe, modifying diatomite with the hydrochloric acid (0.5 N) increases the percentage of the silica (SiO_2) content. The main components of the activated with acid are oxides of Si and Al, and with a real density of 0.550 g/cm^3 and specific surface area, 65.89 m^2/g.

It has been well recognized that the performance (reactivity and selectivity) of a catalyst depends greatly on its dimensions or size. So, our activated diatomite support has been subjected to the granulometric analysis. The particle size distribution is given in Fig. 3.

Figure 3 shown, the main percentage of particle size 0.10-1.40 μm ranges, contains the fractions of 0.136-0.216 μm about 58.55%, 0.216-0.345 μm about 28.25 and 0.345-0.551 μm about 10.35% are presented. To obtain fractions enables a good catalyst support and filterability of the catalyst after hydrogenation, so, acid activated diatomite can be used the catalyst's synthesis.

Then, palladium chloride (0.2 wt.% Pd) supported on activated diatomite (0.2% Pd/D) was prepared by the adsorption method in this work. The morphological structure of the raw diatomite, activated diatomite and 0.2% Pd/D catalyst was studied by the SEM (Fig. 4). Raw diatomite was porous granulated species before pretreatment (a). The SEM micrographs (b) of acid activation (acid activation and followed by calcinations at 500 ºC) showed the original of the pores to be preserved, it can be noticed from the SEM micrographs that diatomite has a highly porous structure which was the main reasons to select this material as a support for preparation of palladium catalyst.

The metal dispersion of was characterized by TEM analysis and from the obtained pictures also average Pd crystallite size was estimated. As it is showed by Fig. 5. Pd-supported diatomite characteristic of mesopouros structures. Palladium particles are well separately dispersed on a catalyst surface and have an average size of 2-8 nm ranges.
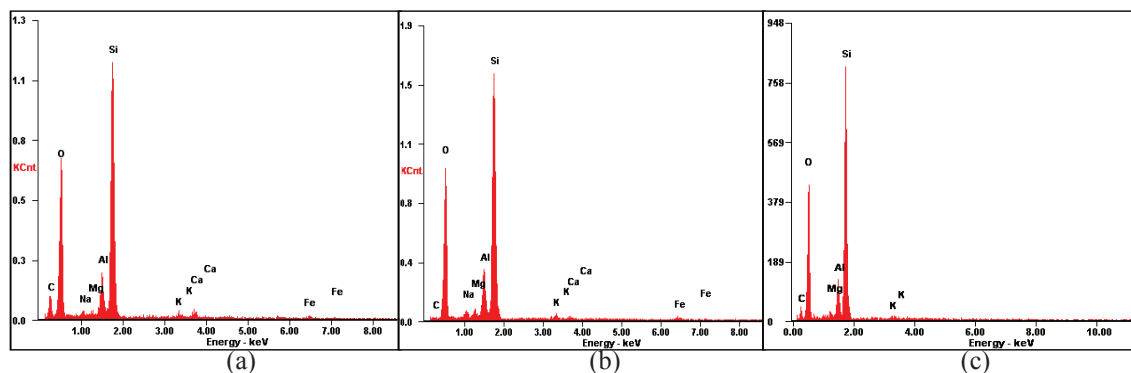
Fig. 2. EDXA spectra of (a) – raw diatomite, (b) – thermally treated diatomite (500 ºC) and (c) – acid activated diatomite.

Table 1
The average of chemical compositions of raw, thermally treated and acid activated diatomite

Samples of diatomite	Chemical content (% weight)						
	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	CaO	K_2O	MgO
D (raw)	74.61	12.97	3.42	3.13	0.54	1.36	2.97
D (500)	78.12	12.52	4.16	1.14	0.28	0.76	2.86
D (500), HCl	83.89	10.81	2.06	0.61	0.11	1.12	0.72

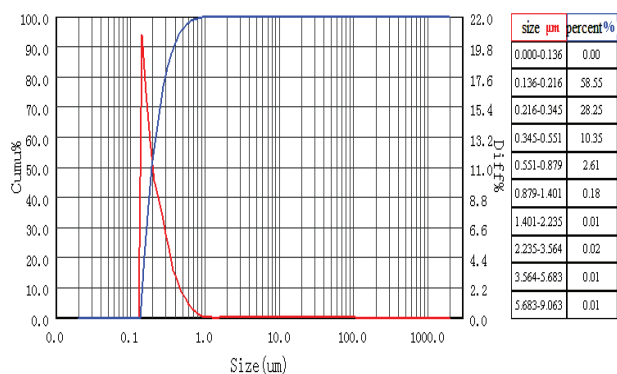| size μm	percent%
0.000-0.136	0.00
0.136-0.216	58.55
0.216-0.345	28.25
0.345-0.551	10.35
0.551-0.879	2.61
0.879-1.401	0.18
1.401-2.235	0.01
2.235-3.564	0.02
3.564-5.683	0.01
5.683-9.063	0.01

Fig. 3. Particle size distribution of the acid activated diatomite.

Testing activity of a synthesized 0.2% Pd/D catalyst in the process of hydrogenation of vegetable oils (sunflower and canola oil)

0.2% Pd/D catalyst was testing for the hydrogenation of sunflower oil, hydrogenation experiments was performed at varying temperatures (70, 90 and 110 ºC), 5 atm pressure in laboratory using the Parr reactor. Industrial testing of 0.2% Pd/D catalyst for hydrogenation of canola oil was carried out at 90 ºC and 5 atm pressure on LTD "Maslo-Del" oil and fat factory (Almaty city, Kazakhstan) and compared to commercial nickel catalyst (Pricat-9910) at 150 ºC, 5 atm pressure.

Testing of the catalyst's performance has been conducted in a laboratory testing reactor and industrial reactor under the following conditions (Table 2).

Table 2
Working conditions of Parr reactor and industrial reactor in the process of oil hydrogenation

	Laboratory reactor (sunflower oil)	Industrial reactor (canola oil)
Type of reactor	Parr reactor-4848	Batch
Capacity (kg)	1	10000
Mass of the oil	60 ml	7500 kg
H_2 pressure (atm pressure)	5	5
Temperature, (ºC) [0.2% Pd/D]	70, 90, 110	90
Temperature, (ºC) [Pricat-9910]	150	150
Agitation (rpm)	600	130

The sunflower and canola oils used in the hydrogenation process have had the following physicochemical characteristics prior to its use (Table 3).

0.2% Pd/D catalyst was laboratorial tested for the hydrogenation of sunflower oil. The hydrogenation activity was monitored by the decay of iodine value (IV) which indicates the level of saturation of double bonds. The fatty acid composition at various temperatures of hydrogenation process is listed in Table 4.
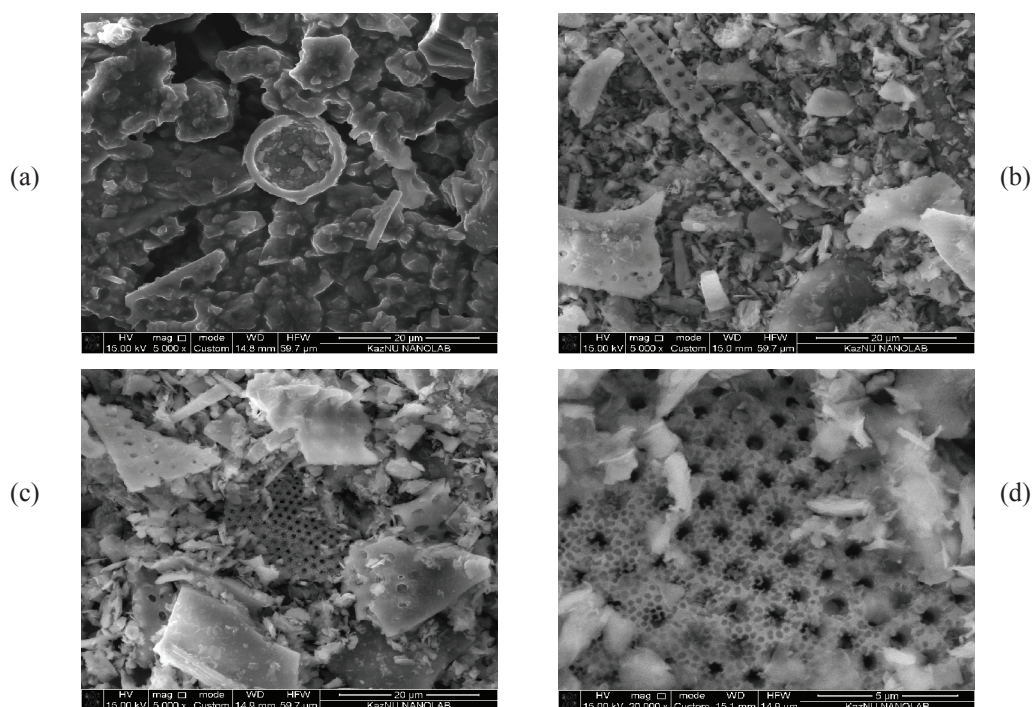
Fig. 4. SEM of the samples: (a) – natural diatomite, (b) – treated diatomite,
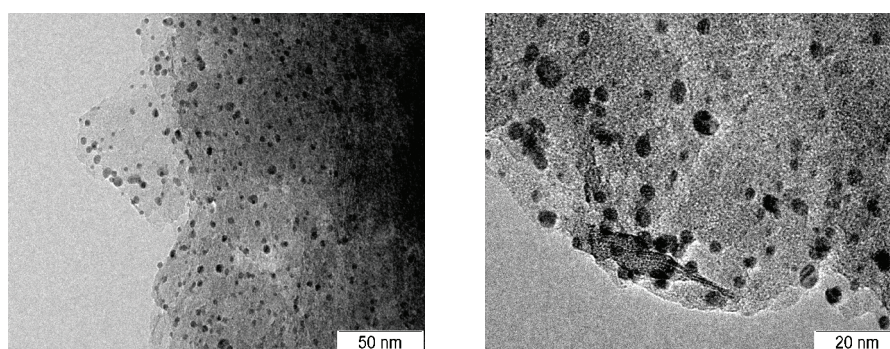(c) – 0.2% Pd/diatomite (×5000) and (d) – 0.2% Pd/diatomite (×20000)

Fig. 5. TEM images for 0.2%Pd/D catalyst.

Table 3
Physico-chemical characteristics of
sunflower and canola oil oils

Parameters	Sunflower oil	Canola oil
Peroxide value (mEq/kg)	0.935	8.7
Acid value (%)	0.23	0.26
Saponification value (mg KOH/g)	190.89	1912
Refraction index	1.4644	1.4639
Iodine value (g I_2/100g)	133	128.9
Fatty acid composition (%)		
$C_{16:0}$-palmitic acid	8.4	6.6
$C_{18:0}$-stearic acid	5.3	3.0
$C_{18:1}$-oleic acid	18.8	38.5
$C_{18:2}$-linoleic acid	63.8	33.2
$C_{18:3}$-linolenic acid	0.7	14.1

Table 4 shows on the composition of the fatty acids produced by hydrogenating sunflower oil over the palladium catalyst high activity lower temperature and during the process the triglycerides of linoleic acid are mainly hydrogenated. The specific isomerization and the formation of conjugated double bonds increased with increasing temperature. Lowering the reaction temperature lowers the trans-isomer produced. For sunflower oil at 70 ºC, reduce the *trans*-isomer content is 13.4%. Typical commercial Ni catalyst operates under commercial reaction condition that is high temperature and the Ni catalyst is not active below 120 ºC. The high temperature operation results in high levels of *trans* fatty acids [7]. Laboratory testing results have shown that palladium catalyst more active and in certain cases have a lower tendency to form trans fatty acids than Ni, at 150 ºC, the *trans*-isomer content is 21.1%.

Table 4
Fatty acid composition of samples during hydrogenation of sunflower oil

Catalysts	t, ºC	Fatty acid composition, %					Trans-isomers, %	IV	MP, ºC
		$C_{16:0}$	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$			
Feedstock	-	8.4	5.3	18.8	63.8	0.7	0.718	133	-16
Pricat-9910	150	9.9.	8.1	59.3	18.6	0.0	21.1	83.5	43.6
0.2% Pd/D	70	8.6	12.0	64.0	12.34	0.05	13.4	72.4	32.2
	90	9.3	11.1	68.7	8.3	0.0	15.2	73.6	33.2
	110	10.6	10.9	63.5	11.1	0.0	17.8	73.7	34.0
	130	10.4	11.8	66.7	7.6	0.4	18.4	71.8	35.2

We also determined the melting point of hydrogenated fat, melting point is a parameter of significant importance for characterizing and developing fats [22]. Fats melting points lower than body temperature can be applied the butter, because they melt completely in the mouth. As shown Table 4, obtained fats using the palladium catalyst, melting points of 32.2-35.2 ºC ranges. And, using the nickel catalyst melting point is 43.6 ºC. Hydrogenated fat obtained on the 0.2% Pd/D catalyst is relatively low observed melting temperature, whereas the melting temperature of hydrogenated fat with nickel catalyst is higher than body temperature.

The solid fat content (SFC) of hydrogenated fats are also determined. SFC is a major concern in food applications, and is generally considered the fingerprint of oils and fats to characterize the physical and sensory properties of foods such as spreadability, texture, firmness and mouth-feel. SFC would be useful for formulating new products and also for authenticating the oil and fat [23]. Quality of food products containing fats and oils strongly depends on SFC that characterizes the crystallization behavior at different temperatures. SFC of hydrogenated fats are presented in Fig. 6.
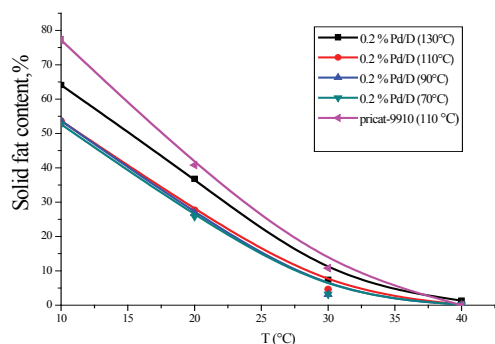

Fig. 6. Solid fat content of hydrogenated oils over 0.2% Pd/D and Pricat-9910 catalysts.

Figure 6 shows the information drawn as SFC profiles hydrogenated oils over 0.2% Pd/D catalyst

(hydrogenation temperature at 70, 90, 110 ºC) melted at about 10 and 30 ºC, respectively. Melting point of hydrogenated oils over Pricat-9910 catalyst melted at 20 and 35 ºC, respectively. The increased SFC during hydrogenation is the result of increase in saturated fat as well as increase in trans-fat isomer contents.

It was canola oil used in industrial pilot hydrogenation. Industrial testing of palladium catalyst for hydrogenation of canola oil was carried out on LTD "Maslo-Del" oil and fat factory (Almaty city). Industrial testing hydrogenation process carried out in 10t of capacity batch reactor at 90 ºC and pressure of hydrogen 0.5 MPa by using 0.2% Pd/D catalyst and compared to commercial nickel catalyst (Pricat-9910) at 150 ºC and 0.5 MPa. The fatty acid composition at hydrogenation process is listed in Table 5 and solid fat content Fig. 7.
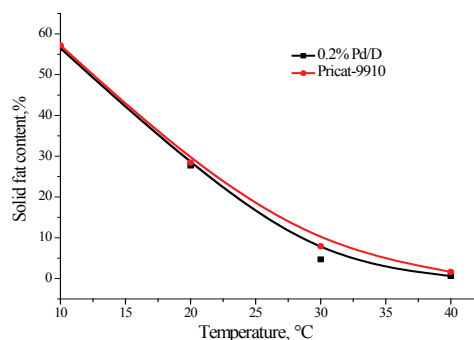

Fig. 7. Solid fat content of hydrogenated canola oil over 0.2% Pd/D and Pricat-9910 catalysts.

On the Table 5, industrial tests and analysis of products shows that low percentage palladium catalyst is able to carry out the process at lower temperature than the commercial nickel catalyst. Hydrogenation at lower temperature and pressure can minimizes the isomerization of a *cis*- to *trans*-isomer double bond conformation. The results of the chromatographic analysis of products show that *trans*-isomers content was reduced at 1.5 times as palladium catalyst is compared with nickel catalyst.

Table 5
The composition of fatty acids partial hydrogenated canola oil over low percentage
palladium catalyst and commercial Ni catalyst (Pricat-9910)

Catalysts	t, ºC	Fatty acid composition, %					*Trans*-isomers, %	IV	MP, ºC
		$C_{16:0}$	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$			
Feedstock	-	6.6	3.0	38.5	33.2	14.1	1.4	128.9	-
Pricat-9910	150	9.5	8.8	65.6	11.3	0.0	20.5	78.5	33.0
0.2% Pd/D	90	8.7	9.9	67.5	5.6	0.0	13.4	72.4	32.6

Figure 7 shows physical parameters of products such as solid fat content obtained from both catalysts are the same. Also, other parameters like melting point and iodine values are the same too. 0.2% Pd/D catalyst is much effective in hydrogenation of canola oil with operates at lower temperature, although this condition reduced the formation of trans fatty acid content.

Conclusion

A low percentage of Palladium catalyst is more effective and highly selective in hydrogenation of sunflower and canola oil. The catalysts, containing palladium, showed activity similar or superior to commercial nickel containing samples in laboratory and industrial tests, Palladium catalysts are active at low temperature of 70 ºC and decreased trans fatty acids in hydrogenation of vegetable oils than nickel catalyst. And, the synthesized 0.2% Pd/D catalyst could be economically beneficial for applications than commercial Ni catalyst.

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