Palladium Catalyst for the Production of Pure Margarine

CATALYST AND NEW NON-FILTRATION TECHNOLOGY IMPROVE PRODUCTION AND QUALITY

By V. I. Savchenko and I. A. Makaryan

Institute of Chemical Physics of the Russian Academy of Sciences, Chernogolovka, Moscow Region, Russia

The production of the fatty base for edible margarines by the hydrogenation of vegetable oils is carried out at high temperatures and has serious disadvantages, among them the toxicity of the nickel catalysts and a fire-hazardous filtration stage. Here, a novel reactor and a new, active and selective, low-loaded palladium catalyst are described which allow vegetable oil hydrogenation to take place at lower temperatures producing high quality, pure hydrogenated fat, free of catalyst. Under these milder conditions, the thermal decomposition of oils and fats does not form secondary products, and heavy metals from the catalyst do not enter the final product. In addition, even lower hydrogenation temperatures can be used with the palladium catalyst, resulting in fat with a low trans-isomer content. The catalyst has been tested successfully in full-scale production. Using an inertial separator in a new reactor, catalyst loss has been eliminated.

In this century margarine has become an important part of the human diet and to some extent has replaced high cholesterol butters. The worldwide annual production of margarines is about 10 million tonnes. Margarine is a multi-component liquid-fat system, and the fatty base consists of modified fats of natural vegetable oils (for instance, sunflower, soybean and rapeseed oils). The main method used to modify natural vegetable oils into the fatty base for margarine is by the selective catalytic hydrogenation of the triglycerides of the unsaturated acids in vegetable oils. This produces hydrogenated fat and *trans*-isomers.

At present the hydrogenation is performed using finely-dispersed nickel catalysts at elevated temperatures (180–230°C), either as a batch process in reactors with stirrers or continuously in a series of mixing reactors. However, under these conditions nickel can react with components of the fat to form fat-soluble salts which may contaminate the food product. If filtration is insufficient, finely-dispersed nickel cat-

alyst may also enter the food product. Moreover, under these severe conditions secondary products may form by thermal decomposition and these could be harmful (some may even be carcinogenic). The process has other disadvantages, such as a high risk of fire during the filtration of the hydrogenated fat from the catalyst and a need to continuously replace catalyst lost during filtration by adding exact doses of fresh catalyst to the reactor. These disadvantages contribute to making the production of pure margarine problematic and some manufactured margarines may contain undesirable levels of nickel.

Nickel Toxicity

The first data on the toxicity of nickel were obtained more than 100 years ago in the Strasbourg Pharmacological Institute (1). Current literature points to the fact that nickel and its salts may cause toxic effects to the kidneys, produce reproductive and organism growth defects, suppress immunity and be cardiotoxic. Later studies have shown that nickel is one of

the most common human allergens and recent work implicates nickel and its salts as carcinogenic to humans, reacting with deoxyribonucleic acid (DNA) and binding the phosphate groups of DNA (1). Hence, it would be desirable if the conventional technology for producing hydrogenated fat for edible margarine was reviewed.

Other concerns involve the soil in which the vegetable oil crop is grown – even soil cultivated without mineral fertilisers and pesticides – which may already be contaminated by heavy metals (such as mercury and lead) and chlorine-containing organics, and it is impossible to avoid their effects. Thus, in modifying vegetable oils for margarine, only technologies which do not add further contamination to the natural raw materials should be examined.

Attempts to Replace Nickel

The main challenge in developing technologies for the production of pure margarines is to find a replacement for the nickel-containing catalyst. One such alternative may be palladium, and several studies have been reported using palladium catalysts to hydrogenate vegetable oils. The first thorough investigations using palladium-based catalysts for vegetable oil hydrogenation were reported by M. Zajcew who hydrogenated large batches of oil (in a reactor of volume ~ 100 litres) and produced about 7 tonnes of hydrogenated fat (2). However, as Zajcew's catalyst (5 per cent palladium/carbon) used about 6.5 g of palladium per 1 tonne of oil, it was considered unprofitable.

Other work on the characteristics of hydrogenation, using palladium on alumina catalyst, has been performed by V. D. Sokol'sky and colleagues (3), and later research has shown that the linolenic and linoleic selectivities, the *trans*-isomer content and the range of fatty products obtained, are similar for palladium and nickel catalysts (4–7). However, when palladium catalysts – developed for other reactions – were used to hydrogenate oils, the attempts were uneconomical. To improve the economics, the amount of palladium consumed needs to be significantly reduced and the palladium needs to be reused or recycled. Some aspects of the oil hydrogenation process also require the development of an optimised dedicated catalyst.

Development of a New Palladium Catalyst

The expertise at The Institute of Chemical Physics of the Russian Academy of Sciences (ICPC RAS) in Chernogolovka, in developing hydrogenation catalysts based on platinum group metals, was utilised for the production of a low-loaded palladium-based catalyst to hydrogenate vegetable oils. The catalyst which was eventually developed gives a highly stable, efficient process with the required product selectivity (8–10). Distinctive features of the hydrogenation have been observed.

The amount of palladium in the catalyst has only a small effect on the hydrogenation rate of vegetable oils, highly purified from catalytic poisons, see Table I. A 100-fold increase in the palladium content in the catalyst and thus

Table I			
Effect of the Palladium Concentration in the Catalyst on the Hydrogenation Rate of Highly-Purified Sunflower Oil			
Pd content in catalyst, wt.%	Ratio oil:Pd by weight	Hydrogenation rate, mol H$_2$ h^{-1}/1 g of catalyst	Specific activity, mol H$_2$ h^{-1}/1 g of Pd
0.005	1000000:1	0.107	2140
0.05	100000:1	0.134	268
0.2	25000:1	0.174	87
0.5	10000:1	0.214	43

Catalyst is Pd/Al$_2$O$_3$, charge of catalyst is 20 g per 1 kg of oil, reaction temperature is 102°C

Table II

**The Effect of Catalyst Particle Size (d)
on the Initial Rate of
Sunflower Hydrogenation**

Catalyst particle size, d, μm	Hydrogenation rate, mol H_2 h^{-1}/ 1 g of catalyst	$1/d \times 10^{4}$, m^{-1}
54–70	0.251	1.62
70–100	0.174	1.19
100–160	0.125	0.79
160–200	0.080	0.56
200–300	0.052	0.41

Catalyst is Pd/Al$_2$O$_3$, oil:Pd ratio is 25000:1
Reaction temperature is 102°C

in the weight ratio oil:palladium, only doubles the hydrogenation rate. The catalyst containing 0.005 weight per cent (wt.%) palladium had the highest specific activity/gram of palladium. Much more activity was shown by catalyst samples containing less than 0.005 wt.% palladium, but the oil was not pure enough to keep the catalyst operation stable, and deactivation followed rapidly. From the initial hydrogenation rates, the slight sensitivity of the reaction rate to the palladium content is retained even for catalysts containing only 0.001 wt.% palladium. Palladium is a very active catalyst for the hydrogenation of triglycerides of unsaturated acids. Other reactions with such high hydrogenation rates are not easy to find.

Investigations on the effect of the particle size of the palladium-based catalyst (characterised by the particle size of the carrier, in the range 50 to 300 µm) at a constant weight ratio, oil:palladium = 25000:1, showed that the hydrogenation rate increases inversely to the particle diameter, see Table II.

The temperature dependence of the hydrogenation rate, see Figure 1, used to determine the activation energy, shows "parallel" curves for two catalyst samples of different particle size. The approximate linearisation of the curves gives the activation energy as ~ 6 kcal mol^{-1}. This value for the activation energy is typical for processes in which a mass transfer is the rate determining step.

Vegetable oil hydrogenation proceeds in a

three-phase system: gaseous hydrogen, liquid reagents (oil and dissolved hydrogen) and solid suspended catalyst, see Figure 2. The scheme assumes the following process stages:

• mass transfer of hydrogen from the gas to the liquid phase;

• mass transfer of hydrogen and hydrogenating oil from the liquid phase to the suspended catalyst particles;

• diffusion of reactants through the pores;

• chemical interaction of reactants on the surface of the catalyst particles;

• mass transfer of reaction products from the catalyst surface to the liquid.

Our investigations show that the hydrogenation reaction with palladium occurs in the diffusion zone and that the activity of the palladium in the kinetic zone is so high that it does not reach its full value under real reaction conditions. Even if conditions for the mass transfer of hydrogen from the gas to the liquid phase are provided, the rate determining step for the reaction is still most likely to be the transfer of hydrogen and oil from the liquid phase to the catalyst surface.

Under these conditions the hydrogenation rate depends mainly on the catalyst outer surface
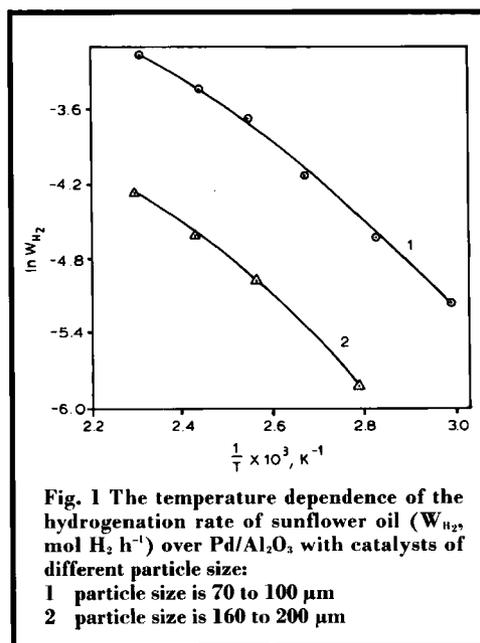

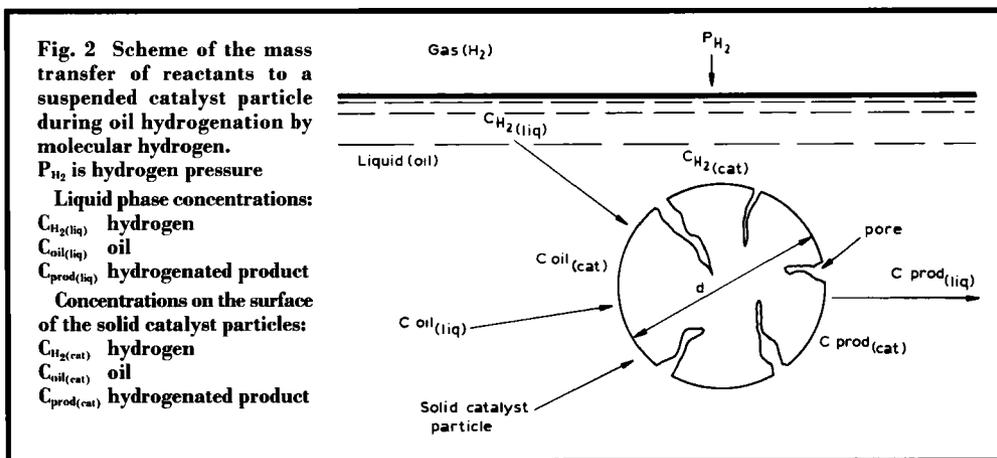**Fig. 1 The temperature dependence of the hydrogenation rate of sunflower oil (W_{H_2}, mol H_2 h^{-1}) over Pd/Al$_2$O$_3$ with catalysts of different particle size:**
1 particle size is 70 to 100 µm
2 particle size is 160 to 200 µm

Fig. 2 Scheme of the mass transfer of reactants to a suspended catalyst particle during oil hydrogenation by molecular hydrogen.

P_{H_2} is hydrogen pressure

Liquid phase concentrations:
$C_{H_2(liq)}$ hydrogen
$C_{oil(liq)}$ oil
$C_{prod(liq)}$ hydrogenated product

Concentrations on the surface of the solid catalyst particles:
$C_{H_2(cat)}$ hydrogen
$C_{oil(cat)}$ oil
$C_{prod(cat)}$ hydrogenated product

Gas (H_2) P_{H_2}

$C_{H_2(liq)}$

Liquid (oil)

$C_{H_2(cat)}$

pore

C oil (cat)

C prod (liq)

C oil (liq)

d

C prod (cat)

Solid catalyst particle

available for the reaction (or the size of the particles) and the amount of catalyst present. Only a small amount of active palladium is needed to activate the small amount of hydrogen required for the reaction (consumption of hydrogen is ~ 5 g per 1 kg of hydrogenating vegetable oil). The oil:palladium ratio only affects the catalyst lifetime, as increasing the amount of active metal in the oil increases the number of centres capable of reacting with the catalyst poisons from the initial oil.

Data on the composition of the fatty acids produced by hydrogenating sunflower oil over the palladium catalyst, at 20 mg Pd per 1 kg of oil and 150°C, are given in Table III. During the process the glycerides of linoleic acid are mainly hydro-genated; the amount of *trans*-isomers increases monotonically and reaches 57.4 per cent when the iodine value (I.V.) = 78.5. (Iodine value is the number of grams of iodine absorbed by 100 grams of fat. As unsaturated fat absorbs iodine, the I.V. is a measure of how much unsaturate is present.) For values of I.V. from 132.1 to 83.7 the increase in stearic acid glycerides is not significant (from 5.6 to 7.3 per cent), but during the subsequent hydrogenation – for I.V. from 83.7 to 78.5 – the amount of stearic acid glycerides noticeably increases from 7.3 to 9.2 per cent. Industrial nickel catalysts also show a similar product distribution.

As *trans*-isomers of hydrogenated fats may be unhealthy to consume (11), we investigated the possibility of using our low-loaded palladium

Table III

The Composition of Fatty Acids Produced by Hydrogenation of Sunflower Oil over Low Percentage Palladium Catalyst

Reaction time, min	I.V.	Fatty acid composition, %				*trans*-Isomer content, %
		18:2	18:1	18:0	16:0	
0	132.1	66.4	20.0	5.6	7.5	0
2.8	122.9	55.8	30.7	5.7	7.2	11.2
7.4	114.7	46.4	40.0	5.8	7.3	18.5
14.6	106.0	36.7	49.4	6.0	7.4	31.9
24.9	90.1	19.2	66.2	6.7	7.4	45.0
32.7	83.7	11.9	73.4	7.3	6.7	51.5
43.8	78.5	8.4	74.4	9.2	7.4	57.4

Charge of Pd is 20 mg per 1 kg of oil, reaction temperature is 150°C
Content of acyl radicals in triglycerides in fatty acids of: linoleic (18:2); oleic (18:1); stearic (18:0); palmitic (16:0)

Table IV

Characteristics of the Hydrogenation of Soybean and Sunflower Oils at Moderate Temperatures

Soybean oil hydrogenation up to I.V. = 95 ± 3							
Temperature, °C	I.V.	Fatty acid composition, %					*trans*-Isomer content, %
		18:3	18:2	18:1	18:0	16:0	
90	92.0	0.8	23.0	58.3	5.9	11.0	21.7
80	95.0	1.0	25.5	56.1	5.4	11.0	20.6
70	93.0	1.0	24.4	56.3	6.4	10.9	19.2
50	97.7	1.3	28.9	51.5	6.2	11.1	14.7
30	96.6	1.2	28.7	51.0	7.1	11.0	12.5

Sunflower oil hydrogenation up to I.V. = 75 ± 2						
Temperature, °C	I.V.	Fatty acid composition, %				*trans*-Isomer content, %
		18:2	18:1	18:0	16:0	
95	73.0	2.2	80.4	11.1	5.2	33.9
70	74.6	2.4	78.0	10.4	5.6	29.4
45	76.9	9.4	70.4	12.4	6.6	21.8

Charge of Pd is 20 mg per 1 kg of oil
Linolenic acid (18:3); linoleic acid (18:2); oleic acid (18:1); stearic acid (18:0); palmitic acid (16:0)

catalyst to produce a hydrogenated product with a low *trans*-isomer content. Table IV shows that lowering the reaction temperature lowers the proportion of *trans*-isomers produced. By keeping activity high for the palladium catalyst, down to a temperature of 30 to 45°C, the unsaturated acids of soybean oil could be hydrogenated, but with decreased *cis* → *trans* isomerisation. For soybean oil at I.V. values = 95 ± 3 and 30°C, the *trans*-isomer content is 12.5 per cent, and for sunflower oil at I.V. = 75 ± 2 and 45°C, the *trans*-isomer content is 21.8 per cent (at 150°C the *trans*-isomer content is ~ 60%). Thus, by optimising the catalyst composition and the hydrogenation conditions (by hydrogenating at low temperatures) a hydrogenated fat with a much lower *trans*-isomer content can be produced.

Technical Regulations were developed for the preparation of this palladium catalyst and a pilot plant was built at ICPC RAS to synthesise the catalyst. The plant could produce 20 kg of catalyst per operation (an operation lasted for about 4 to 6 hours). Catalysts were successfully tested at the Moscow Fat Plant in 1988 using an industrial autoclave of volume 12 m³ and around 70 tonnes of edible hydrogenated fat were produced there.

Tests show that the palladium catalyst has the following advantages over conventional nickel catalysts:

• The catalyst components (palladium and carrier) do not react with the initial oil or its hydrogenation products and do not enter the product; thus no contamination occurs. This results in margarines of high edible quality and purity.

• The hydrogenation is performed at temperatures of 120 to 140°C (compared to the conventional 180 to 230°C), thus secondary products do not form as a result of thermal decomposition of oils and fats and there are no harmful admixtures in the final food product.

• The reduced hydrogenation temperatures produces hydrogenated fat of low *trans*-isomer content.

• The catalyst has a low palladium content with only 1 to 2 g of palladium being needed to hydrogenate 1 tonne of vegetable oil. This amount may be lowered further by reducing the contamination of the initial oil.

• Recent work has shown that the catalyst may be regenerated many times (12) and noble metal can be recovered from the spent catalyst and used in new syntheses. Thus, the consumption of fresh palladium is further reduced.

As the catalyst is finely dispersed, "non-filtration" methods have been developed to replace the filtration stage so as to separate the catalyst and reaction products.

New Technology for Preparing Pure Margarines

The palladium-containing catalysts used for oil hydrogenations were usually developed for other applications, with finely divided palladium supported on active carbon being the most commonly used.

However, vegetable oil hydrogenation has a number of distinctive features, and requires an optimised, dedicated catalyst. The catalyst must be able to produce hydrogenated fat with optimised fatty acid and glyceride contents (it must give the correct linolenic and linoleic selectivities, the correct ratio for the rates of hydrogenation and isomerisation of acyl groups, and the required intra- and intermolecular distribution of fatty acids in triglycerides). It must also be resistant to the compounds in vegetable oils which poison palladium catalysts. These compounds are phosphatides, gossypol, sulfur-containing organics and others, found in various amounts in vegetable oils. The deactivation to the catalyst they cause depends on the amount of contamination in the oil.

The hydrogenation of oils, highly purified from admixtures of catalyst poisons, proceeds rapidly, even over a dedicated catalyst containing less than 0.005 per cent palladium, at an oil: palladium ratio of $> 10^7:1$. The resistance of the catalyst to poisons during multiple use, gives a standard for the consumption of palladium/unit of final product.
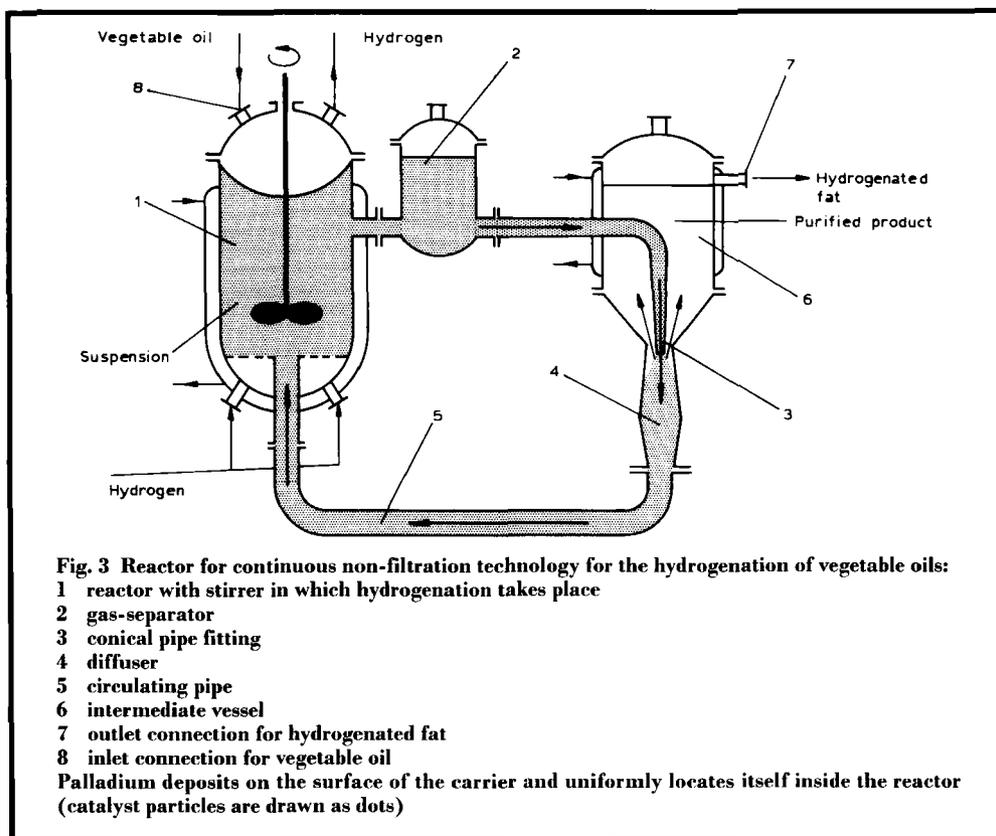
The catalyst is cost effective if palladium is consumed at a rate of 1 to 2 grams/tonne of product, based on a palladium price of U.S.$200 per oz. As more recently the palladium price has increased to U.S.$350 per oz, the consumption of palladium must be further lowered. This has been taken into account, as modern large-scale industrial hydrogenations often regenerate and reuse palladium, so decreasing the consumption of fresh palladium by 10–20 times.

Instead of using conventional industrial catalysts supported on carbon carriers, we selected an active alumina support of precisely known particle size. This allowed continuous and batch-operated technologies with multiple catalyst use to be developed. The use of active alumina made it possible to design catalysts having optimised hydrogenation characteristics. The solid particles remain continuously in the reaction volume; catalyst is not lost with the reaction products and filtration-free technology was developed. The method used to prepare the catalyst allowed modifications in palladium content and fractional content to be made, see Table V.

Palladium chloride "P" and active alumina "A" were the main components used in synthesising the catalyst, possibly promoted

Table V
Catalyst Modifications

With respect to palladium content		With respect to fractional composition			
Modification	Palladium content, wt.%	Modification	Fraction content, wt.%		
			less than 60 μm	from 60–140 μm	over 140 μm
AP-005	~ 0.05	D	at least 95	-	-
AP-01	~ 0.1				
AP-02	~ 0.2	F	not over 5	at least 93	not over 2
AP-2	1.8–2.0				

A is active alumina, P is palladium chloride, D is dispersed and F is fractionated

Fig. 3 Reactor for continuous non-filtration technology for the hydrogenation of vegetable oils:
1 reactor with stirrer in which hydrogenation takes place
2 gas-separator
3 conical pipe fitting
4 diffuser
5 circulating pipe
6 intermediate vessel
7 outlet connection for hydrogenated fat
8 inlet connection for vegetable oil
Palladium deposits on the surface of the carrier and uniformly locates itself inside the reactor
(catalyst particles are drawn as dots)

by microadditions of boron in boron:palladium ratios of 2×10^{-4} to 5×10^{-5} (10). Vegetable oils were hydrogenated in continuous and batch variants. The palladium consumption was about 1.5–2.0 g tonne^{-1} of product for sunflower and soybean oils, but was higher for rapeseed oil purified by conventional industrial technology.

Development of Non-filtration Technology

The nickel catalysts used for hydrogenating vegetable oils are highly dispersed powders as this is the only form which gives the necessary activity. However, this produces a "black hydrogenated fat" (a mixture of hydrogenated oil and reduced catalyst) which requires purification. The purification is a bulky, laborious, fire hazardous and low efficiency filtration process, usually performed with frame-type filters. Even then catalyst microparticles and dissolved nickel are

not completely captured. For further entrapment, additional treatment of the hydrogenated product by an adsorbent is needed.

Attempts to use tablet-shaped nickel catalysts in a fixed-catalyst bed apparatus were not very successful as activity was low, and increased hydrogen pressure was necessary. This also decreased the selectivity of the linoleic acid hydrogenation.

Most of the literature on vegetable oil hydrogenation over palladium catalysts describes the use of fine catalyst powders. As powder catalysts have higher activity, the consumption of palladium/unit of product should be reduced. However, in practice, the same problems occur in separating hydrogenated product and catalyst for palladium as for highly dispersed nickel, and as the palladium cannot be reused, its consumption is high.

In order to separate off the Pd/Al$_2$O$_3$ catalyst

suspension, "non-filtration" methods (for example, sedimentation and inertia) were developed at ICPC RAS. The decrease in catalyst activity, due to increased particle size, and the lower oil:palladium ratio used for the hydrogenation are compensated for by having a reusable catalyst. The product is a "white hydrogenated fat" free of catalyst particles.

Two methods of hydrogenation using fractionated palladium catalysts were developed:
• a batch method with catalyst sedimentation
• a continuous method in a novel reactor which combines the hydrogenation process and the separation of the hydrogenated product and catalyst particles, and ensures that catalyst is continuously present in the reactor without loss on withdrawal of the products.

The continuous method uses finely-grained catalyst of given dispersion, modification F, see Table V. The reaction mixture, containing the catalyst particles, circulates continuously around the reactor at a high speed, see Figure 3. The catalyst is separated from the reaction products at the place where a sudden expansion in the circulating stream occurs. Separation is achieved using the inertial motion of the catalyst particles, and the product stream is withdrawn in an opposite direction to the motion of the solid catalyst particles.

The reactants involved in the process are continuously fed into reactor 1, while to achieve separation, part of the reaction mixture is moved out of the gap between diffuser 4 and pipe fitting 3 into the intermediate vessel 6 in an opposite direction to the suspension. Due to inertial forces the catalyst particles continue moving with the circulating suspension, and therefore practically almost never get into the liquid stream withdrawn into intermediate vessel 6.

Both methods ensure that the palladium catalyst undergoes multiple operations during vegetable oil hydrogenation. The "white hydrogenated fat" is produced without a filtration stage and the "non-filtration" technology is highly effective for margarine production.

Multiple Use of the Palladium Catalyst

Palladium catalyst on a fractionated carrier remains in the system when hydrogenated fat is removed and allows the catalyst to be reused for further hydrogenation. Data from successive hydrogenations of ten batches of sunflower oil over the same catalyst are shown in Table VI. At first the hydrogenations have almost identical characteristics but as the batch number increases, the hydrogenation rate gradually decreases, thus the hydrogenation time increases. If the initial oils were purer, then more batches of oil could be hydrogenated.

Table VI							
Characteristics of Hydrogenated Fats Produced during Consecutive Hydrogenations of 10 Batches of Sunflower Oil (up to I.V. = 78 ± 2)							
Batch number	Hydrogenation time, min	I.V.	Fatty acid composition, %				*trans*-Isomers content, %
			18:2	18:1	18:0	16:0	
1	47	79.8	9.3	74.0	8.8	7.3	54.7
2	47	79.2	9.1	73.8	9.7	6.8	55.2
3	58	79.9	10.0	72.8	9.6	7.0	56.1
4	62	76.7	7.8	73.5	10.6	6.9	58.4
5	62	77.0	8.4	72.6	11.4	7.0	57.9
6	66	76.7	8.9	71.3	11.9	7.3	57.6
7	68	77.8	9.1	72.1	11.2	7.0	56.9
8	81	77.1	8.9	71.7	12.1	6.7	57.3
9	84	76.3	7.6	73.4	11.2	7.2	58.5
10	92	76.5	8.4	72.1	12.1	6.8	58.8

Charge of Pd is 20 mg per 1 kg of oil
Linoleic acid (18:2); oleic acid (18:1); stearic acid (18:0); palmitic acid (16:0)

Regeneration of spent catalyst has also been examined, but no suitable solvent or method was found to remove the catalytic poisons from the catalyst surface. However, after treating spent catalyst with palladium-containing compounds, the activity may be restored to its original value and several further hydrogenations can be achieved. Impregnation of the supports with palladium-containing compounds can be repeated many times. Finally, spent catalyst with a high palladium content is formed from which palladium can be extracted and reused in fresh catalyst.

Increasing the Oil Decontamination Index

Hydrogenations performed under mild conditions (120–140°C) over the palladium-based catalyst form almost no undesirable secondary products by the thermal decomposition of oils and fats; free fatty acids do not form and the final produce of "white hydrogenated fat" does not require additional refining and deodorisation, which is essential in conventional technologies.

However, in order to ensure that the palladium consumption is low, the initial preparation of the vegetable oils prior to hydrogenation needs to be improved, as palladium is very sensitive to catalyst poisons. We have found that the purification stages should remain the same, namely: alkali refining, washing, drying and deodorisation, but the purity of the refined vegetable oils must be higher and free of certain compounds, especially those containing sulfur. If the refined oil is purer, the cost of the palladium and its contribution to the cost of the final product will be less.

Conclusions

A new highly selective catalyst containing small amounts of palladium has been developed for the hydrogenation of vegetable oils. The main principles of the hydrogenation process have been worked out and new highly efficient and cost effective technology, using the catalyst, has been successfully tested for the production of pure edible margarines. Together, the new catalyst and novel reactor design are able to achieve the full-scale production of margarines.

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Acoustic Catalysis in Palladium

Acoustic excitation applied to thin noble metal films on single crystals enhances the catalytic reactions occurring over these surfaces (1).

Now work in Japan has described the different kinetic behaviours on the two faces of a single LiNbO₃ crystal covered with a thin Pd film during ethanol oxidation using resonant acoustic oscillations (RO) (2). RO causes an anomalous increase in catalytic activity. Activation energy falls from 156 to 36 kJ mol⁻¹ on the positively polarised, (+)Pd, surface, and to zero on the negatively polarised Pd surface. Oxygen is strongly adsorbed on the (+)Pd surface.

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