Winged bean oil contained about half as much behenic acid (22:0) as reported by Cerny et al. (11), and contains more behenic acid than is found in both soybean and peanut oils. Behenic acid is a long chain saturated fatty acid with 22 carbon atoms and a melting point of 80 C, and it is chemically related to erucic acid, having one double bond. The long-term nutritional effect of consuming oils containing erucic acid has puzzled experts for some time.

Despite the poor digestibility of behenic acid, its toxic effects were not observed when children were fed undefatted winged bean flour containing 160-180 mg of behenic acid/kg body weight/day (3). Behenic acid is found mainly in the unsaturated fraction which is lost during industrial refining of crude edible oil. The contents in arachidic, behenic and lignoceric acids in peanut oil were also found to be half that of arachidic and behenic acids together in winged bean seed oil.

Cerny (3) suspected the presence of an unusual fatty acid, tentatively identified as parinaric acid on the basis of relative retention times. Parinaric acid is found as a constituent of balsam (*Impatiens balsamina*) and edible drupes (*Parinarum laurinum*) (12). Parinaric acid apparently was not isolated before from edible legume seeds (13); it is unsuitable fo for use in human diet. Parinaric acid, a conjugated 18:4, would not coelute with 20:1. Further examination of this fraction using the method of plotting the log of retention times against carbon number showed conclusively, against earlier speculations (3), that the unusual fatty acid is eicosenoic acid. This disagrees with Cerny's tentative result (3), which identified this fraction as parinaric acid. Because parinaric acid is toxic, the acceptance of winged beans and their oil as foods was hindered. The presence of eicosenoic acid, however is in agreement with more recent research by others (14).

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Kinetics of Nickel Catalyst Poisoning

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ABSTRACT

Hydrogenation was done in a "dead-end" type of reactor with automatic recording of hydrogen absorption. In order to determine the poisoning rates of various nickel catalysts with phospholipids, allyl isothiocyanate (AITC), free fatty acids, sodium soaps and products of lipid oxidation, these poisons were added to the reaction system while the reaction was approaching the highest rate. The kinetic curves show that, at the moment of inhibitor addition, the reaction rate decreases immediately; for AITC, the reaction is even stopped for a certain period of time. This observation proves inhibitors are adsorbed at the metal surface immediately after introduction to the system. In some cases, after decreasing the reaction rate, we have observed subsequent acceleration of the reaction that may result from depoisoning processes at the catalyst surface.

INTRODUCTION

The effects of trace amounts of substances (poisons) in oils subjected to metal catalyzed hydrogenation on the kinetics of process has been discussed in many papers devoted to the inhibitory action of sulfur and phosphorus compounds (1-14). Much less information is available on the subject of free fatty acids, sodium soaps (1,14-15) and the products of partial oil oxidation (14). In papers dealing with those compounds emphasis is mainly on the degree of metal catalyst deactivation by phospholipids, allyl isothiocyanate (AITC), free fatty acids, sodium soaps and products of lipid oxidation, whereas the kinetics of catalyst poisoning, the subject of this paper, has not been studied.

EXPERIMENTAL PROCEDURES

Materials

Refined, bleached and deodorized soybean oil was used as starting material for hydrogenation. The oil had a peroxide value (PV) of 1.5 me O_2/kg and contained 0.1% free fatty acids (FFA), 5 μg/g phospholipids (P) and 2 μg/g sodium soaps (Na).

Three types of catalyst were used: the 533-unsupported, formate type, containing 10.3% Ni (Fat Factory, Gdańsk); Nysel DM-3-supported, containing 24.8% Ni (Harshaw); and RCH 55/5-FS-supported, containing 21.0% Ni (Hoechst). The RCH catalyst was stored for a long period of time and inactivated since the experiment required a catalyst with a long induction period. Fresh RCH catalyst generally has short induction period and higher activity.

Catalyst inactivators—phospholipids, AITC, free fatty acids, their sodium soaps and the products of partial oil

TABLE I

Inhibitor Concentration in Soybean Oil

Inhibitor	Catalyst		
	Nysel DM-3	RCH 55/5-FS	533
	Inhibitor concentration		
Phospholipids (P)	23 μg/g	40 μg/g	23 μg/g
AITC (S)	23 μg/g	23 μg/g	23 μg/g
Free fatty acids	6%	6%	6%
Sodium soaps (Na)	25 μg/g	45 μg/g	15 μg/g
Lipids oxidation products (O_2)	62.0meO_2/kg	62.0meO_2/kg	62.0meO_2/kg

oxidation—were prepared according to the procedure reported earlier (14).

Hydrogenation

Hydrogenations were carried out in a "dead-end" type of reactor with automatic recording of hydrogen absorption under the following constant conditions of hydrogenation: oil sample, 50 g; catalyst concentration, 0.1% Ni; temperature, 160 ± 0.5 C; stirring rate, 2700 rpm; atmospheric pressure.

The catalyst was placed first in a special container above the surface of oil, inside the reactor; after process conditions stabilized and the oil was saturated with hydrogen, the catalyst was introduced into the oil. This moment was considered the starting point for the reaction.

The curves traced by the recorder express the volume (cc) of absorbed hydrogen by 1 g of hydrogenated oil in relation to the reaction time. Therefore, they illustrate the reaction kinetics and we shall refer to them as kinetic curves. The time interval measured from the moment of catalyst introduction to the moment of beginning of hydrogen absorption by oil was called the induction period.

In order to determine the rate of nickel catalyst poisoning, the poisons were introduced into the reaction system in the initial phase of hydrogenation, when mainly polyenic acids were reduced and the reaction rate reached highest values. For simplicity, the inhibitors were added in all cases when 1 g of hydrogenated oil absorbed 10 cc of H_2.

Catalyst inactivators, such as phospholipids, free fatty acids and sodium soaps, were placed in a special container inside the reactor before introduction to the reacting system. Oil solutions of AITC and oxidized oil were directly injected at an appropriate moment through a silicon rubber septum. For comparison, identical hydrogenations were carried out by initially introducing the same quantities of inhibitors into the oil before the catalyst addition.

In all our studies, the inhibitors, except for lipid oxidation products, were used in concentrations within the concentration range which results in the reduction of catalyst activity by 40-60%. The application of poison concentrations that gives exactly the same decrease of catalyst activity was relatively difficult to carry out in practice. Inhibitor concentrations used in our studies are shown in Table I.

RESULTS AND DISCUSSION

Kinetic curves of soybean oil hydrogenations with inhibitors introduced into the oil (concentrations shown in Table I) before and during the reaction are shown in Figs. 1-5. In our studies on the kinetics of nickel catalyst poisoning we have concentrated on the phase of soybean oil hydrogenation with hydrogen absorption of ca. 40 cc per 1 g of oil. In this range of hydrogen absorption, we calculated the reaction rate constants according to formula I:

$$-d(IV)/dt = k(IV), \qquad [I]$$

neglecting induction periods and the periods when the reaction was stopped, as in the case of AITC (Fig. 2). Hydrogenation rate was variable, particularly when inhibitors were introduced to the reacting system. Therefore, reaction rate constants were calculated for subintervals of hydrogen absorption.

The results obtained for hydrogenations of initial soybean oil (without inhibitor addition) and oil with inhibitors added at various stages of the process are shown in Table II.

An analysis of hydrogenation kinetics (Figs. 1-5, Table II) shows an immediate and marked decrease of the reaction results from the introduction of inhibitors into the system during the absorption of hydrogen by oil; sometimes the reaction is stopped completely (AITC addition, e.g., see Fig. 2). Therefore, inhibitors are adsorbed at once. This, however, does not signify that the process proceeds at

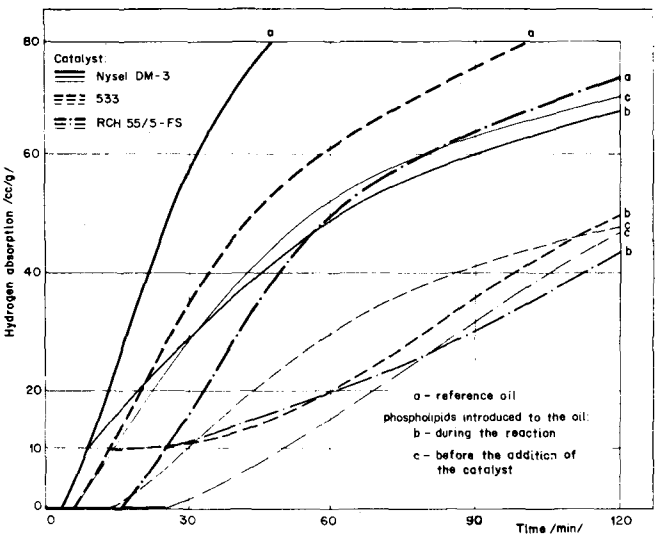

FIG. 1. Kinetic curves for reference soybean oil and soybean oil with phospholipids introduced to the reaction system at various stages of the process.

the same rate for different catalyst inactivators. For example, free fatty acids and their sodium soaps show a constant decrease of hydrogenation rate (Table II). In turn, when AITC is added to the reaction system, the reaction is stopped, which suggests that all active centers at the catalyst surface are blocked.

We have observed an interesting phenomenon in the analysis of reaction rate changes (Table II, Figs. 1,2 and 5) during hydrogenations with some inhibitors introduced in the period of strong hydrogen absorption by oil. After the addition of phospholipids, products of oil oxidation or AITC, the reaction rate accelerated after the initial stage of strong retardation, except for the reaction carried out in the presence of phospholipids and Nysel DM-3 catalyst.

The process described above (retardation and subsequent acceleration of the reaction rate) suggests there is deblocking of active centers of the catalyst. It is therefore a self-depoisoning of the catalyst. This effect may result from many factors which are difficult to define. One possible explanation is the transformation of inhibitor molecules on the catalyst and the formation of less poisonous forms or species which desorb themselves from the catalyst surface. For example, in sodium soaps, their hydrolyses may form FFA which, as shown in our earlier papers (14), are less poisonous than sodium salts. It is also possible that inhibitor molecules (or products of their transformations) migrate to the catalyst surface not involved in the process of triglyceride hydrogenation (capillaries and pores with small diameters).

The most notable effect of catalyst depoisoning is observed after the introduction of AITC to the reaction system (Fig. 2). This effect is independent of the catalyst type: the reaction is completely stopped for a relatively long time, e.g., ca. 30 min for RCH catalyst, and then there is a significant increase in the reaction rate. The reaction rate constant after 62 min from the renewed initiation of the reaction already equals 0.0079 min^{-1}. Therefore, in the AITC experiment, the catalyst depoisoning may result, apart from the earlier-mentioned transformation or diffusion on the catalyst surface, from the reaction of a sulfur

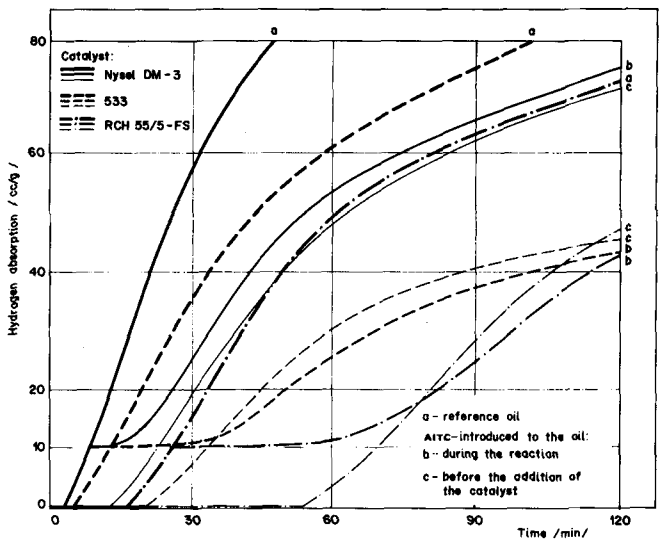

FIG. 2. Kinetic curves for reference soybean oil and soybean oil with AITC introduced to the reaction system at various stages of the process.

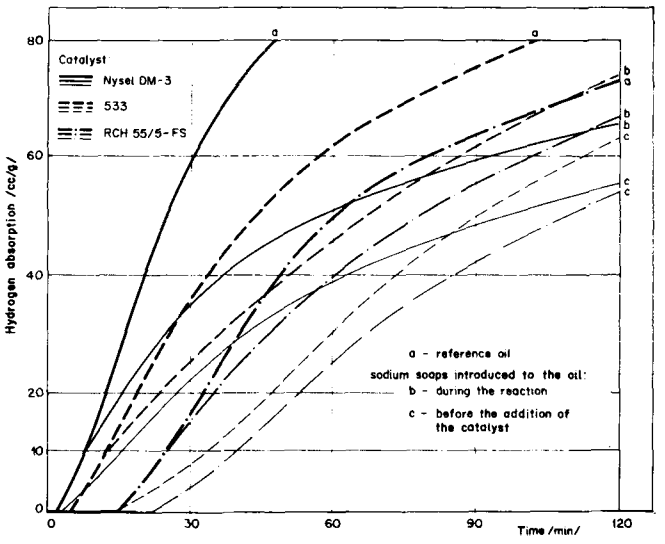

FIG. 4. Kinetic curves for reference soybean oil and soybean oil with sodium soaps introduced to the reaction system at various stages of the process.

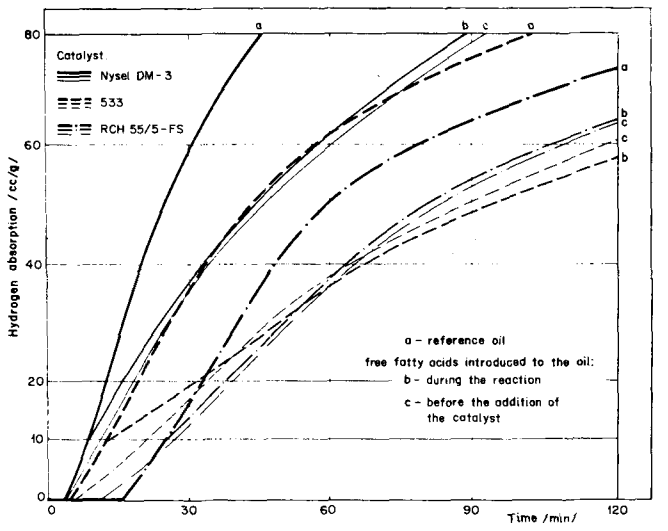

FIG. 3. Kinetic curves for reference soybean oil and soybean oil with free fatty acids introduced to the reaction system at various stages of the process.

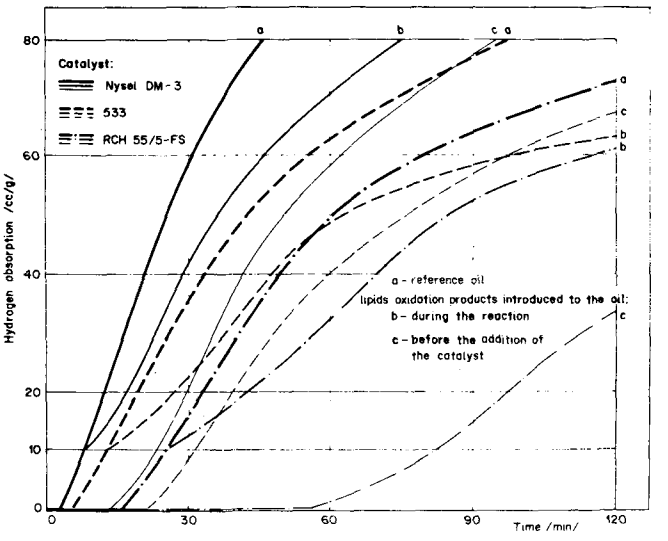

FIG. 5. Kinetic curves for reference soybean oil and soybean oil with the products of its partial oxidation introduced to the reaction system at various stages of the process.

TABLE II

Hydrogenation Rate Constants for Reference Soybean Oil and Oil with Inhibitors Introduced to the Reaction System at Various Stages of the Process

Oil	Inhibitors introduced to oil	Catalyst: Nysel DM-3 Hydrogen absorption cc/g	Nysel DM-3 k min^{-1}	RCH 55/5-FS[a] Hydrogen absorption cc/g	RCH 55/5-FS[a] k min^{-1}	533 Hydrogen absorption cc/g	533 k min^{-1}
Reference	—	0-10	0.0151	0-10	0.0084	0-10	0.0101
		10-40	0.0163	10-40	0.0109	10-40	0.0119
With the addition of phospholipids	Before the addition of the catalyst	0-10	0.0094	0-10	0.0034	0-10	0.0047
		10-40	0.0100	10-40	0.0046	10-40	0.0061
	During the reaction time	0-10[b]	0.0151	0-10[b]	0.0084	0-10[b]	0.0101
		10-20	0.0078	10-20	0.0024	10-15	0.0012
		20-30	0.0071	20-30	0.0034	15-20	0.0031
		30-40	0.0075	30-40	0.0046	20-30	0.0044
						30-40	0.0054
With the addition of AITC	Before the addition of the catalyst	0-10	0.0076	0-10	0.0047	0-10	0.0060
		10-40	0.0105	10-40	0.0077	10-30	0.0067
						30-40	0.0048
	During the reaction time	0-10[b]	0.0151	9-10[b]	0.0084	0-10[b]	0.0101
		10-15	0.0044[c]	10-15	0.0024[c]	10-15	0.0025[c]
		15-20	0.0083	15-20	0.0042	15-20	0.0055
		20-30	0.0120	20-30	0.0059	20-30	0.0059
		30-40	0.0128	30-40	0.0079	30-40	0.0040
With the addition of free fatty acids	Before the addition of the catalyst	0-10	0.0105	0-10	0.0050	0-10	0.0050
		10-40	0.0108	10-40	0.0073	10-40	0.0067
	During the reaction time	0-10[b]	0.0151	0-10[b]	0.0084	0-10[b]	0.0101
		10-20	0.0106	10-20	0.0078	10-20	0.0052
		20-30	0.0102	20-30	0.0075	20-30	0.0050
		30-40	0.0100	30-40	0.0075	30-40	0.0047
With the addition of sodium soaps	Before the addition of the catalyst	0-10	0.0063	0-10	0.0044	0-10	0.0050
		10-40	0.0070	10-40	0.0059	10-20	0.0065
						20-40	0.0071
	During the reaction time	0-10[b]	0.0151	0-10[b]	0.0084	0-10[b]	0.0101
		10-20	0.0089	10-20	0.0082	10-20	0.0074
		20-30	0.0075	20-30	0.0080	20-30	0.0068
		30-40	0.0075	30-40	0.0065	30-40	0.0068
With the addition of lipids oxidation products	Before the addition of the catalyst	0-10	0.0076	0-5	0.0021	0-5	0.0062
		10-40	0.0148	5-10	0.0038	5-10	0.0096
				10-40	0.0057	10-40	0.0100
	During the reaction time	0-10[b]	0.0151	0-10[b]	0.0084	0-10[b]	0.0101
		10-20	0.0091	10-20	0.0051	10-20	0.0058
		20-30	0.0140	20-30	0.0064	20-30	0.0089
		30-40	0.0150	30-40	0.0081	30-40	0.0108

[a]The catalyst with decreased activity due to prolonged storage. The reaction catalyzed by fresh catalyst was characterized by constant k in the absorption range 10-40 cc H_2/g of oil equal to 0.0210 min^{-1} and the induction periods equal to 1 min.

[b]0-10 - reaction without the addition of inhibitors (reference oil). Introduction of inhibitor at the absorption 10 cc H_2/g of oil.

[c]After the introduction of AITC, the reaction rate was equal to zero for a period of time different for different catalysts.

compound with metal, yielding Ni_3S_2. Such modified surfaces exhibit some activity in fat hydrogenation (16-18). We have found that during hydrogenations of oil containing AITC, more *trans* configuration double bonds are formed than during the reaction without that inhibitor. This fact, in some sense, supports the theory of nickel sulfide formation, since sulfide catalysts are characterized by a higher degree of geometrical isomerization of fatty acid double bonds than the metal catalyst (17,18).

The changes described for the reaction rate, e.g., when the reaction was stopped or slowed down and in some cases accelerated, are not observed when inhibitors are present in oil before the catalyst addition (Figs. 1-5, Table II). This indicates that inhibitor transformations and possible modification of surface occur during the induction period. Therefore, we observe the overlapping of catalyst activation with its inactivation.

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On the Formation of Degradation Products from the Pyrolysis of Tall Oil Fatty Acids with Kraft Lignin

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ABSTRACT

Mixtures of tall oil fatty acids and kraft lignin from southern pine wood were pyrolyzed at 160 C and 280 C with or without exclusion of oxygen. In addition to fatty acids of various chain lengths and aromatic degradation products from lignin, a number of homologous *n*-alkylbenzenes were formed (ca. 1.5%) and characterized by gas chromatography-mass spectrometry. The possible ways of formation of the latter from fatty acids are discussed briefly.

INTRODUCTION

The tall oil distillation and fractionation process is carried out at temperature regions above 200 C (1). Because partially demethylated lignin is present in the tall oil distillation residue (pitch) (2), lignin, though modified, must be present in the raw tall oil before the distillation process. To determine substances which possibly could have been produced during tall oil distillation by reaction with still present lignin, similar reaction conditions to those in the technical distillation process were applied to a mixture of tall oil fatty acids and kraft lignin. By this procedure it was possible to obtain more information on possible reaction products of tall oil fatty acids and kraft lignin. The composition of the tall oil fatty acid fraction which was used in all experiments is shown in Table I (3).

EXPERIMENTAL PROCEDURES

Pyrolysis of Tall Oil Fatty Acids with Kraft Lignin at 280 C

Kraft lignin (5 g) and tall oil fatty acids (17.5 g) were heated to 280 C and kept at this temperature for 30 min. After cooling, the mixture was shaken with chloroform and filtered. The insoluble residue was ca. 1 g. The clear solution was distilled at a maximum temperature of 265 C at 2000 Pa. The fraction distilled at this temperature was 5.2 g. One gram of the distillate was taken up in 10 ml methanol and methylated with 100 ml of a solution of freshly prepared diazomethane in ether. The solvent mixture was evaporated, and the residue was dissolved in ether and analyzed by gas chromatography-mass spectrometry. The gas chromatographic separation was performed using a 25 m OV-101 WCOT glass capillary column, and the mass spectra were recorded on a Hewlett-Packard quadrupole mass spectrometer system HP 5992A. The construction of the apparatus allowed connection of the end of the column directly to the ion source. The list of detected compounds is given in Table II.

Pyrolysis of Tall Oil Fatty Acids with Kraft Lignin at 160 C

Kraft Lignin (5 g) and tall oil fatty acids (17.5 g) were heated to 160 C and kept at this temperature for 30 min. After cooling, the mixture was extracted with chloroform (ca. 50 ml) and filtered to yield 5.5 g insoluble residue. Additional procedures were the same as described above. The list of detected compounds is given in Table III.

Pyrolysis of Tall Oil Fatty Acids with Kraft Lignin at 280 C under Nitrogen

The same reaction procedures were used as described above. This distillation was performed at 0.1 Pa, and one part of

TABLE I

Composition of the Tall Oil Fatty Acids Used in All Experiments

Compound	%
hexadecenoic acid	1.0
hexadecanoic acid	6.5
heptadecanoic acid	1.5
octadecatrienoic acid	0.5
octadecadienoic acid	ca. 39.0
octadecenoic acid	ca. 40.0
octadecanoic acid	2.0
other fatty acids	ca. 2.0
total fatty acids	92.5
isopimaric acid	1.5
pimaric acid	0.7
dehydroabietic acid	0.5
other diterpenoid acids (including abietic acid)	2.0
total diterpenoid acids	4.7
pinosylvin dimethylether	ca. 3.0
other unsaponifiables	ca. 1.5