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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 vegetable oils. This paper reviews new hydrogenation processes such as electrocatalytic hydrogenation, precious catalyst hydrogenation, and supercritical fluid state hydrogenation, which have shown promising results for the reduction of *trans* fatty acids below the level of 8%. This paper also reviews the recently introduced hydrogenation technique for high accumulation of conjugated linoleic acids, beneficiary functional components. The hydrogenated vegetable oils with high quantity conjugated linoleic acid might provide the possibility for the utilization of hydrogenated oils as health-promoting food ingredients.

## Introduction

Hydrogenated vegetable oils have been used since the 1st part of the 20th century to expand the application of vegetable oils in foods. Vegetable oils are the most important edible oils, representing more than 70% of edible oils in the world. Hydrogenated vegetable oils provide distinctive flavor, crispness, creaminess, plasticity, and oxidation stability to common foods. But hydrogenated oils contain high quantities of *trans* fatty acids, which are associated with an increased risk of cardiovascular disease by raising the level of serum low-density lipoprotein cholesterol and decreasing the level of high-density lipoprotein cholesterol (Mensink and Katan 1990; Troisi and others 1992; Willet and others 1993; Ascherio and others 1994; Judd and others 1994; Aro and others 1997). Desci and Koletzko (1995) have also reported positive associations between the intake of *trans* fatty acids and inhibition of arachidonic acid biosynthesis, which is essential for normal child growth and development.

Due to increased concern about *trans* fatty acids on health, a federal task force has suggested that *trans* fatty acids should be added to or included with saturated fatty acids on labels as a separate class and to implement a threshold proportion of *trans* fatty acids for health claims (Feldman and others 1996). Legislation in the United States, approved in June 2003, requires the nutrition facts panel on all food labels to indicate *trans* fat content by January 1, 2006. Health concerns about *trans* fatty acids have led to interest in interesterification, fractionation, or blending of saturat-

ed and polyunsaturated oils as an alternate method to hydrogenation—alternatives that could be more costly than conventional hydrogenation. The alternative methods do not easily produce the desirable physical and chemical properties of oils suitable for manufacturing the broad ranges of oil products such as confectionery, margarines, and shortenings. Therefore, the alternate methods could not easily replace the hydrogenation of vegetable oils. Hydrogenation is still a viable choice for food manufacture if *trans* fatty acids can be substantially reduced during the hydrogenation processes. New hydrogenation processes such as electrocatalytic hydrogenation (Yusem and Pintauro 1992; Yusem and others 1996; An and others 1998a, 1998b, 1999; Mondal and Lalvani 2003), precious catalyst hydrogenation (Hsu and others 1986; Berben and others 2000a, 2000b; Wright and others 2003), and supercritical fluid state hydrogenation (Marcher and others 1999; Macher and Holmqvist 2001; King and others 2001) have been reported to reduce *trans* fatty acids in hydrogenated vegetable oils. New hydrogenation methods to produce health-promoting hydrogenated vegetable oils containing high quantities of conjugated linoleic acids have been reported also (Jung and Ha 1999; Jung and others 2001, 2002; Ju and others 2003).

This paper reviews the use of electrocatalytic hydrogenation, precious metal catalysts hydrogenation, and supercritical fluid state hydrogenation to reduce *trans* fatty acids of hydrogenated oils. Also reviewed are the hydrogenation conditions that increase conjugated linoleic acid in hydrogenated oil.

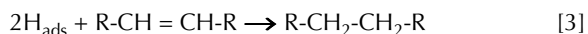
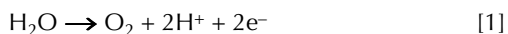
## Electrocatalytic hydrogenation

Conventional hydrogenation uses a nickel catalyst and hydrogen gas at high temperatures of 140 to 230 °C. The high hydrogenation temperature produces high *trans* fatty acids in hydrogenated oils. A low temperature electrocatalytic hydrogenation would

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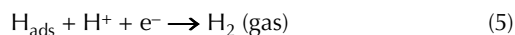
be an alternative method for the production of hydrogenated edible oils low in *trans* fatty acids. Low temperature electrocatalytic hydrogenation uses an electrically conducting catalyst such as Raney nickel or platinum black as a cathode. Electrocatalytic hydrogenation has been used to produce a variety of organic compounds such as aromatic compounds, phenols, ketones, nitro-compounds, dinitriles, and glucose (Pintauro and Bontha 1991; Robin and others 1990; Miller and Christensen 1978; Cyr and others 1990; Song and Pintauro 1991; Park and others 1985, 1986). It has also been successfully used to produce hydrogenated oils with low *trans* fatty acid content (Yusem and Pintauro 1992; Yusem and others 1996; An and others 1998a, 1998b, 1999; Mondal and Lalvani 2003).

The electrochemical reactor contains a cathode for reduction reactions and an anode for oxidation reactions. Atomic hydrogen is generated on the catalytically active cathode surface by the reduction of protons or water molecules through electrolytic reactions in the electrical hydrogenation (Eqs. 1 and 2). The hydrogen atoms adsorbed ( $H_{ads}$ ) on the catalytically active cathode surface react with the double bonds of fatty acids for the formation of saturated fatty acids (Eq. 3). The process eliminates dissociation and mass transfer resistances of molecular hydrogen thereby increasing the reaction rates.



The absorbed atomic hydrogen concentration on the catalyst surface can be controlled by the applied current. This allows low temperature and low-pressure conditions during hydrogenation. Hydrogenation at low temperature and pressure minimizes the isomerization of a *cis* to *trans* double bond.

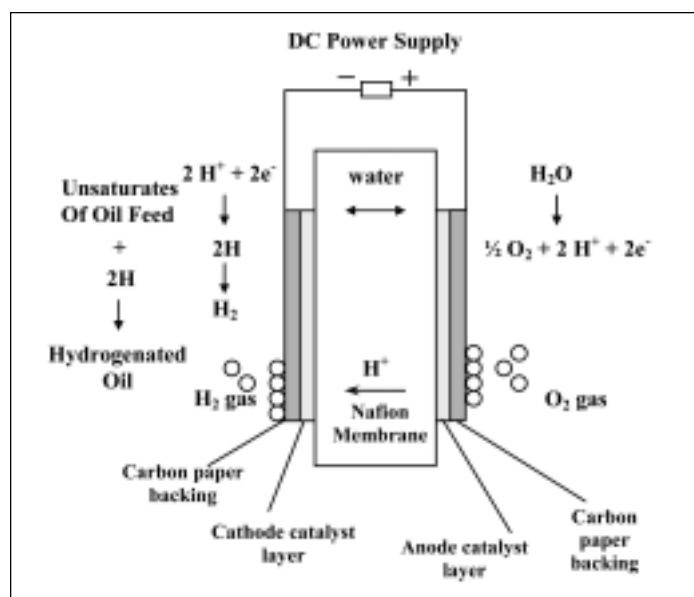
Molecular hydrogen gas ( $H_2$ ) could be formed either by the chemical combination of 2 adsorbed hydrogen atoms or by the electrochemical reduction of adsorbed hydrogen (Eqs. 4 and 5). However, the molecular hydrogen gas does not participate in reducing the double bonds of fatty acids in the electrochemical hydrogenation. Thus, the formation of molecular hydrogen gas is an unwanted side reaction that consumes current but does not affect the product yield. When the double bonds are nearly hydrogenated, the molecular hydrogen gas evolution rate increases. The common problem of high molecular hydrogen ( $H_2$ ) evolution in electrochemical reactors starts when 25% to 50% of double bonds in oils is hydrogenated.



Yusem and Pintauro (1992) and Yusem and others (1996) have reported that soybean oil can be electrochemically hydrogenated at atmospheric pressure, a constant current density between 0.1 to 0.45 A/cm<sup>2</sup> and a low temperature of 70 °C using laboratory-scale axial and radial-flow undivided cells containing a Raney nickel powder cathode. In this electrochemical Raney nickel reactor system, a two-phase reaction medium was used, where soybean oil was dispersed in a water/t-butanol solvent with tetraethylammonium *p*-toluenesulfonate as the supporting electrolyte. Hydrogenation current efficiencies, which measure the oil hydrogenation rate to the total rate of atomic hydrogen production, are in the range of 50% to 100% for apparent current densities of  $1.0 \times 10^{-2}$  to  $2.0 \times 10^{-2}$  A/cm<sup>2</sup> at the 20% to 40% oil concentration in a water/t-butanol solvent with tetraethylammonium *p*-tolu-

enesulfonate as the supporting electrolyte. The stearic acid and *trans* fatty acid levels of electrochemically hydrogenated oil are significantly lower than those of conventionally hydrogenated oil with gaseous molecular hydrogen. Yusem and Pintauro (1997) designed the radial flow-through Raney nickel powder electrocatalytic hydrogenation reactor and performed research on simulation and economic analysis of electrocatalytic soybean oil hydrogenation. The cost for the production plus raw material of electrocatalytic process was 16% greater than that for the conventional hydrogenation (Yusem and Pintauro 1997). A drawback of this electrochemical Raney nickel reactor system was the use of nonfood grade t-butanol for stabilizing emulsion and supporting electrolyte of tetraethylammonium *p*-toluenesulfonate for the reasonable ionic conductivity in the water/alcohol phase.

An and others (1998a) introduced a different method of electrochemical hydrogenation of edible oils using a solid polymer electrolyte reactor, which has previously been used in the hydrogenation of organic compounds (Ogumi and others 1981, 1988). Because solvent or emulsion is not required in this reaction system, it avoids the main drawback of the electrochemical Raney nickel reactor—the use of nonfood grade t-butanol for stabilizing emulsion and supporting electrolyte of tetraethylammonium *p*-toluenesulfonate. An and others (1998a) conducted electrochemical hydrogenation of edible oils in a solid polymer electrolyte reactor composed of an RuO<sub>2</sub> powder anode and either a platinum-black or palladium-black powder cathode that were hot-pressed as thin films onto the opposing surfaces of a Nafion cation exchange membrane. The solid polymer electrolyte reactor has been used for the hydrogenation of soybean, canola, and cottonseed oils, and with mixtures of fatty acids and fatty acid methyl esters at a constant supplied current density of 0.1A/cm<sup>2</sup> and temperatures between 50 and 80 °C. The solid polymer electrolyte reactor consists of separate anode and cathode chambers that are separated by a thin, hydrated, cation-exchange membrane. The thin, hydrated, cation-exchange membrane of precious metal catalyst powder anode and cathode are fixed to opposing faces of the membrane to form a membrane electrode assembly (Figure 1). Water is circulated past the back side of the anode, where water molecules are oxidized to O<sub>2</sub> gas and protons (H<sup>+</sup>), according to Eq. 1. The pro-



**Figure 1—Principles of operation of a solid polymer electrolyte reactor for the electrochemical hydrogenation of oil (adapted from An and others 1998a).**

tons from water oxidation migrate through the ion-exchange membranes under the influence of the applied electric field to the cathode catalyst components of the membrane electrode assembly, where the protons are reduced to atomic and molecular hydrogen (Eqs. 2, 4, and 5). Water and oil phases are separated by a hydrated polymeric cation-exchange membrane. An and others (1998a) reported that the hydrogenated oils with 60 to 105 IV had higher stearic acid and lower *trans* fatty acid content than those of conventionally nickel hydrogenated oils. Platinum black powder cathode was more effective for the reduction of *trans* fats than palladium black powder cathode at similar iodine values. The *trans* fatty acids of hydrogenated oil with 66 to 115 IV by a platinum black cathode were below 4%, while the *trans* isomer content of hydrogenated oil with 61 to 105 IV by palladium black cathode was 6.5% to 10.5%. The *trans* fatty acids of hydrogenated oils with 61 to 105 IV by conventional nickel catalyst were 20% to 40%. The stearic acid of hydrogenated oil by platinum black cathode was slightly higher than that of the oil hydrogenated by palladium black cathode.

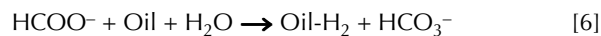
An and others (1998b) further studied the effects of various hydrogenation factors such as cathode catalyst, catalyst loading, the cathode catalyst binder loading, current density, and reactant flow rate on the current efficiency of oil hydrogenation. The current efficiency of different cathode catalysts was in the decreasing order of Pd > Pt > Rh > Ru > Ir. The oil hydrogenation current efficiency with palladium black powder cathode decreased with increasing current density. Current pulsing for frequencies in the range of 0.25 to 60 Hz had no effect on current efficiencies. The combination of increased oil feed flow rate and inserted nickel turbulence promoter into the oil stream increased the current efficiency of oil hydrogenation.

An and others (1999) also reported the effects of cathode designs and reactor operation conditions on hydrogenation selectivity. They increased oil mass transfer into and out of the palladium black powder cathode layer by the combination of increasing the porosity of the cathode carbon paper/cloth backing material, increasing the oil feed flow rate, and inserting a turbulence promoter into the oil feed flow channel. The increased oil mass transfer in the palladium black powder cathode catalyst layer decreased the concentration of stearic acid but increased the concentration of *trans* fatty acids in the hydrogenated oil. The electrodeposited secondary metal (Ni, Cd, Zn, Pb, Cr, Fe, Ag, Cu, or Co) on palladium black powder cathode increased the selectivities of linolenate, linoleate, and oleate and decreased the formation of stearic acid in the hydrogenated oil (An and others 1999).

Warner and others (2000) reported that electrochemically hydrogenated oils produced by a solid polymer electrolyte reactor with Pd cathode catalyst have higher oxidative stability and lower hydrolysis than the Ni catalyst hydrogenated oils. In room odor evaluations of heated oils at frying temperature at 190 °C, Ni catalyst hydrogenated soybean oil showed strong undesirable characteristics of hydrogenation, notably waxy, sweet, flowery, fruity, and/or crayon-like aromas. However, the electrochemically hydrogenated soybean oils showed only weak hydrogenation aroma, indicating that the hydrogenation aroma/flavor would be much less detectable in foods fried in the electrochemically hydrogenated oils.

Mondal and Lalvani (2003) introduced a novel electrochemical hydrogenation of vegetable oil using a hydrogen transfer agent of formic acid and a nickel catalyst. An emulsion of oil and water containing formic acid and nickel, placed in the cathode compartment of an electrolysis cell and subjected to an electrical current, was hydrogenated at temperatures as low as 45 °C. The *trans* fatty acid content of the canola oil hydrogenated at 45 °C was significantly lower than that of the hydrogenated edible oils by conventional Ni hydrogenation at high temperature and high partial

pressure of hydrogen gas. Mondal and Lalvani (2003) hypothesized that the reduction of double bonds occurred via a chemical reaction between the formate ion and oil at the surface of the hydrogenation catalyst (Eq. 6). The oxidized form of the formate ion (bicarbonate ion) was then reduced electrochemically at the cathode, resulting in regeneration of the formate ion (Eq. 7).



This hydrogenation induced the slight hydrolysis of oil owing to low pH (pH 1.5) of the oil/formate/formic acid reaction mixture. This reaction system requires the preparation of emulsion, and the oil separation should be done at the end of reaction.

### Precious metal catalysts hydrogenation

Ni catalysts are most commonly used for vegetable oil hydrogenation in conventional hydrogenation. Ni catalysts offer high-activity, tailored linoleic acid and linolenic acid selectivity, low cost, and easy removal from oils by filtration. The nickel catalyst isomerizes the natural *cis* double bonds to *trans* double bonds during hydrogenation.

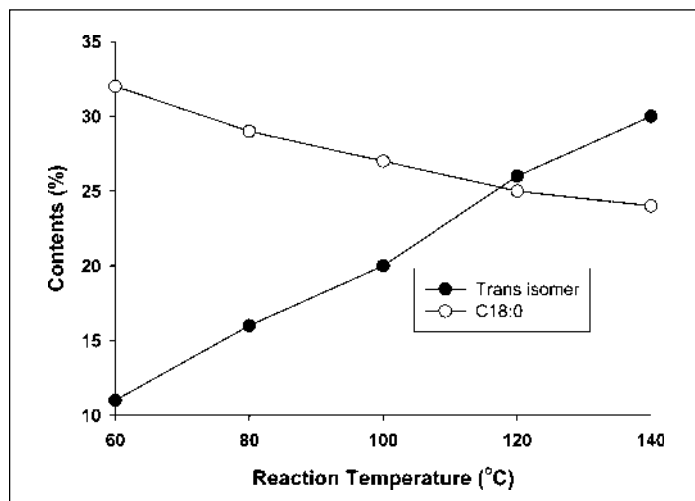
The *trans* fatty acids of hydrogenated vegetable oil by precious metal catalysts were lower than those of hydrogenated oil by nickel catalysts. Nickel catalysts are not very active below 120 °C. Precious metal catalysts, on the other hand, are active at the low temperature of 70 °C. Precious metal catalysts at low temperatures decreased *trans* fatty acids in the hydrogenated vegetable oils. Palladium, platinum, and ruthenium were the most potential precious metal catalysts for the hydrogenation of vegetable oils. Each metal catalyst has different characteristics in selectivity, reactivity, and *trans* isomerization during hydrogenation of vegetable oils. It has been generally accepted that platinum catalysts produce the least amount of *trans* fatty acid during hydrogenation.

The modified palladium catalysts, which are a partially deactivated palladium-on-carbon catalyst by silver and bismuth, showed improved selectivity over the palladium on carbon alone (Zajcew 1960a). Riesz and Weber (1970) used barium sulphate as a carrier for palladium and decreased the *trans*-isomer formation without affecting the activity or selectivity greatly. Ahmad and others (1979) studied the hydrogenation of soybean oil with 1% to 10% palladium-on-carbon at hydrogen pressures between ambient and 70 psi and at temperatures between 80 °C and 160 °C. If palladium is deposited on the exterior of the carbon for the easy access of triglyceride molecules, its selectivity and activity were superior to those of nickel, even at temperatures at which nickel is inactive. Ray (1985) reported the effects of the hydrogenation rate, *trans*-isomer formation, and selectivity on the hydrogenation of soybean oil with palladium-on-carbon catalyst. The author reported that palladium catalyst did not have any advantage on the *trans* fatty acid formation or hydrogenation selectivity over nickel catalysts. Hsu and others (1986), on the other hand, found that palladium black was far superior to nickel catalyst or palladium-on-carbon in lowering the *trans* fatty acids in hydrogenated canola oil. At 250 psi of hydrogen pressure and 50 °C of reaction temperature, hydrogenation with 560 ppm of palladium-on-carbon produced 30.2% *trans* fatty acids, but that with palladium black produced 19% *trans* fatty acids in the hydrogenated canola oil with about 68 IV. Hsu and others (1988) also reported that hydrogen pressure has the most significant effect on the formation of *trans* fatty acids during the hydrogenation with palladium black. The effects of 150 psi and 750 psi hydrogen on the *trans* fatty acid content of canola oil with IV 53 hydrogenated at 90 °C and 560 ppm palladium black showed that 150 psi and 750 psi hydrogen

pressure produced 42.8% and 18.7% *trans* fatty acids, respectively. High pressure and low temperature decreased the formation of *trans* fatty acids during the hydrogenation of canola oil (IV 115) with palladium black. Hsu and others (1988) reported that the hydrogenated oil of IV 74 with 50 ppm palladium black at 750 psi hydrogen pressure and 70 °C reaction temperature had only 9.4% *trans* fatty acids. In general, it was found through the review of previously published papers that palladium forms *trans* fatty acids at a similar level with conventional nickel catalyst. Palladium black, however, produced considerably lower *trans* fatty acid than nickel catalyst.

Wright and others (2003) reported the effect of Ni catalyst addition to palladium black on the *cis* selectivity and the hydrogenation activity for canola oil. The addition of 100 ppm nickel to palladium black increased the hydrogenation activity significantly without any effect on *cis* selectivity of 50 ppm palladium black catalyst at 70 °C and 754 psi. Wright and others (2003) explained that the increased activity of the palladium/nickel system over palladium alone was attributed to the adsorption of catalyst poison from the oil by Ni.

Berben and others (2000a) studied the effects of palladium and platinum catalysts on the formation of *trans* fatty acids and saturated fatty acids during hydrogenation of soybean oil at 60 °C, 102 psi, and 50 or 65 ppm precious metal catalysts. The fatty acid compositions of the hydrogenated oil with palladium were similar to those hydrogenated with nickel. The dropping points of the hydrogenated oils with palladium catalyst were higher than the nickel-catalyzed products. The authors also reported that palladium catalysts did not give any benefits in reducing *trans* fatty acid content. However, platinum catalyst lowered the *trans* isomer formation in the hydrogenated oil. The amount of saturated fatty acids by platinum catalyst hydrogenation was higher than that of hydrogenated oil with nickel or palladium. Platinum catalyst on narrow pore carbon support was more effective in reducing *trans* fatty acids than platinum catalyst with a wide pore carbon support (Berben and others 2000a). The amount of *trans* fatty acids and saturated fatty acids varied with the hydrogenation temperatures in platinum or other catalyst hydrogenation. As the hydrogenation temperature increased, the *trans* fatty acids increased, but saturated fatty acids decreased. Figure 2 shows the effects of hydrogenation temperature on the formation of *trans* fatty acids and saturated fatty acids in hydrogenated oils with 70 IV with platinum on wide pore carbon support. The hydrogenated oil with 69.6 IV that

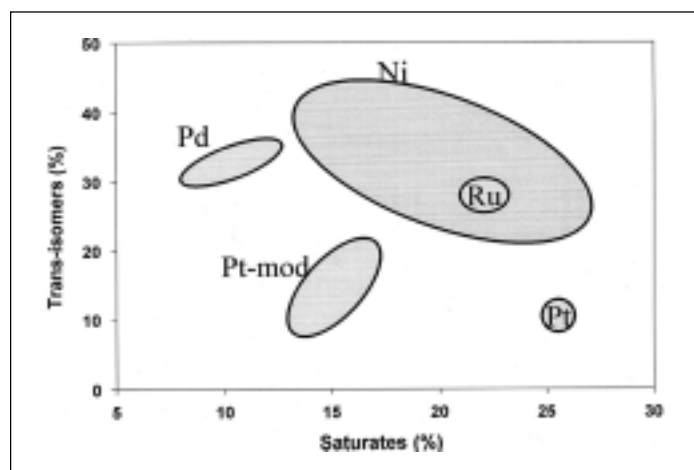


**Figure 2—Effects of temperature on the *trans* fatty acids and saturated fatty acids during hydrogenation with platinum catalyst (adapted from Berben and others 2000b)**

was produced with platinum on wide pore carbon support at the low temperature of 60 °C and high hydrogen pressure of 102 psi, contained 10.9% *trans* fatty acids. The authors reported that further reduction of *trans* fatty acids in hydrogenated oil was obtained by hydrogenation with platinum catalyst on narrow pore carbon support. The hydrogenated oil with 68 IV that was produced with platinum on narrow pore carbon support at the low temperature of 60 °C and high hydrogen pressure of 102 psi, contained only 7.7% *trans* fatty acids.

Berben and others (2000b) studied the effects of various precious metal catalysts on the formation of *trans* fatty acids during hydrogenation of soybean oil at 60 °C, 147 psi hydrogen pressures, and a precious metal loading between 100 and 400 ppm. Both the palladium and the ruthenium on carbon support showed the same amounts of *trans* fatty acids and saturated fatty acids in the hydrogenated oil of 100 IV by nickel catalyst. Palladium catalyst had more hydrogenation selectivity with less saturated fatty acids than ruthenium. Platinum catalyst greatly decreased the formation of *trans* fatty acids in the hydrogenated oils, however, the amounts of saturated fatty acids in hydrogenated oils with platinum was much higher than those of hydrogenated oils with nickel, palladium, or ruthenium. The *trans* fatty acids and saturated fatty acids in hydrogenated oil with 100 IV by platinum on alumina support were 5.4% and 17.6%, respectively. However, the *trans* fatty acids and saturated fatty acids in hydrogenated oil with 100 IV by Ni catalyst were 18.8% and 6.8%, respectively. Berben and others (2000b) produced hydrogenated oil with low saturated fatty acids and *trans* fatty acids by adding ammonia to the catalyst as a reaction modifier. Ammonia addition to palladium catalyst forms very low saturated fatty acids and high *trans* fatty acids in a hydrogenated oil with 100 IV. Ammonia addition to platinum catalyst greatly decreased the formation of both saturated fatty acids and *trans* fatty acids. The amounts of *trans* fatty acids and saturated fatty acids in 100 IV hydrogenated oil by a combination of ammonia and platinum on alumina support were only 6.6% and 6.8%, respectively. Figure 3 summarizes the *trans* fatty acids and saturated fatty acids in hydrogenated soybean oil with 70 IV at various hydrogenation conditions and with various catalysts and/or modifiers.

Conventional hydrogenation produces hydrogenated oils containing 25% to 45% *trans* fatty acids. Hydrogenation with precious metal catalyst could produce hydrogenated oils containing less than 8% *trans* fatty acids, indicating that this technique is



**Figure 3—Effects of precious metal catalysts and modifiers on the *trans* fatty acids and saturated fatty acids of hydrogenated soybean oil with IV 70 (adapted from Berben and others 2000a)**

promising for lowering the *trans* fatty acids. The catalyst amount used in the precious metal catalyst hydrogenation was about 50 ppm, which is at the level of 1/10 to 1/40 of nickel catalyst in conventional hydrogenation. The hydrogenation with precious metal catalyst takes a longer time than conventional nickel hydrogenation, due to its extremely low reaction temperature and low dose of catalyst used in precious metal catalyst hydrogenation. At conventional hydrogenation, it takes less than 40 min to reach to IV 70. However, with precious catalyst, it takes about 100 to 160 min to reach the IV 70 (Berben and others 2000a, 2000b). If the precious catalyst could be easily retrieved from the hydrogenated oils and be reusable, it could be economically beneficial. Unfortunately, the reusability of the precious metals after retrieving from the hydrogenated oils has not been reported.

### Supercritical fluid state hydrogenation

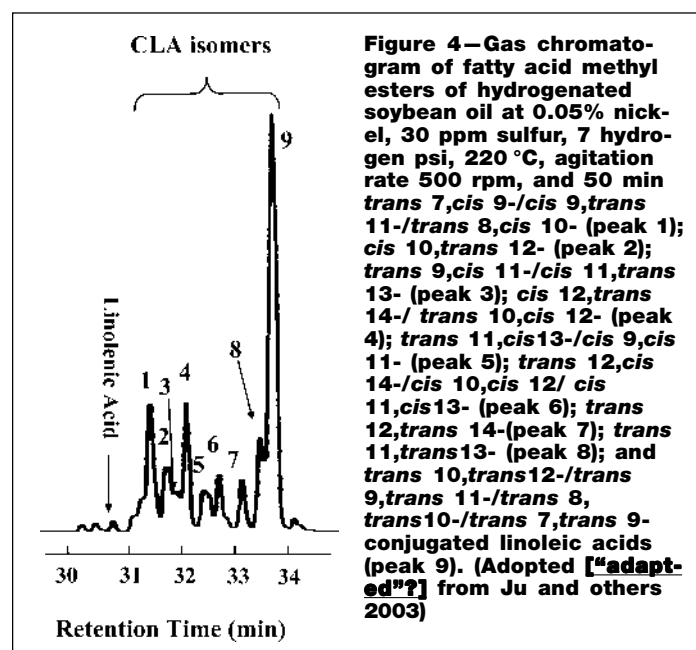
Supercritical fluid state hydrogenation has been recently introduced to improve the hydrogenation of vegetable oils. Conventional Ni hydrogenation is taking place in a three-phase reaction system of hydrogen gas phase, liquid oil phase, and solid catalyst phase. One of the most important hydrogenation rate determining factors is the mass transfer of hydrogen gas to liquid oil near the catalyst surface for hydrogenation. Supercritical fluid state improves hydrogen transfer to the catalyst surface during hydrogenation by providing a good homogeneous phase. The improved mass transfer would increase the hydrogenation reaction rate and decrease the formation of *trans* fatty acids. Several investigators have shown the efficacy of conducting hydrogenation of oleochemicals and vegetable oils using supercritical carbon dioxide or propane as a solvent hydrogenation (Marcher and others 1999; Macher and Holmqvist 2001; King and others 2001). King and others (2001) studied the hydrogenation with conventional nickel catalyst under the supercritical carbon dioxide at temperature from 120 to 140 °C and hydrogen pressure up to 2000 psi. The supercritical carbon dioxide hydrogenation with nickel catalyst reduced the formation of *trans* fatty acids. The hydrogenated soybean oil with 82 IV under supercritical carbon dioxide condition contained 6.4% *trans* fatty acids. Macher and others (1999) studied the hydrogenation of fatty acid methyl ester of rapeseed oil using supercritical propane with a 3% palladium on aminopolysiloxane in a microscale continuous fixed-bed reactor. The hydrogenated oil with IV 70 produced at 92 °C, a hydrogen pressure of 58 psi, and a residence time of 40 ms, contained 3.8% *trans* fatty acids. Macher and Holmqvist (2001) hydrogenated palm oil in near-critical and supercritical propane using a continuous fixed bed reactor with 1% palladium on carbon. The hydrogenated palm oil under the near-supercritical and supercritical conditions showed high reaction rates. At 120 °C and a residence time of 2 s, fully hydrogenated palm oil was obtained. However, the catalysts showed strong signs of deactivation very early in the hydrogenation, possibly due to the impurities in the feedstock and/or to coke formation. Further additional data are needed to clarify the phase behavior of the reaction mixture and optimal conditions for the minimization of *trans* isomer formation in the supercritical fluid state hydrogenation with precious metals (Macher and Holmqvist 2001).

### Hydrogenation for conjugated linoleic acids

Conjugated linoleic acids are a group of natural linoleic acids with a conjugated double bond. Conjugated linoleic acids have been reported to prevent or cure cancer (Ha and others 1987; Liew and others 1995; Ip and others 1996), atherosclerosis (Lee and others 1994), and type II diabetes (Houseknecht and others 1998). Conjugated linoleic acids may regulate cytokines produc-

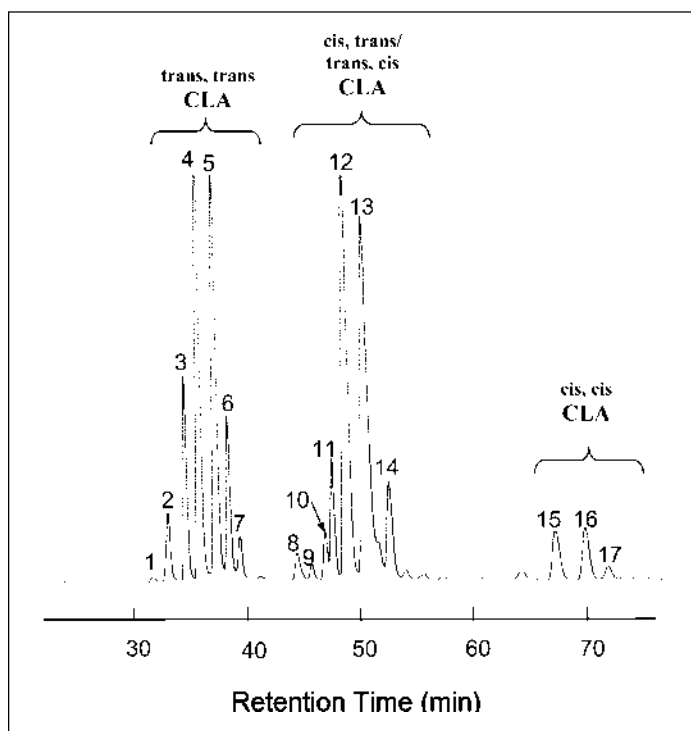
tion to strengthen muscle and bone activity in humans (Cook and others 1993). Fat partitioning activity of conjugated linoleic acids reduces fat synthesis in mice and abdominal circumference in humans (Park and others 1999; Riserus and others 2001). Conjugated linoleic acids are abundant in dairy products and meats from ruminant animals (Ha and others 1989; Chin and others 1992; Shantha and others 1992; Kim and Liu 2002; Boylstone and Beitz 2002). Ha and others (1989) reported high levels of conjugated linoleic acids in cheeses and milk. Chin and others (1992) reported that milk, butter, cheese, yogurt, or meats from ruminants has 3 to 8 mg conjugated linoleic acids (CLA)/g fat. Vegetable oils contained very low levels of CLA, ranging from 0.1 mg conjugated linoleic acids/g coconut oil to 0.7 mg conjugated linoleic acid/g safflower oil (Chin and others 1992). Banni and others (1994) carried out a series of HPLC/UV/MS analyses to characterize the fatty acids with conjugated dienes in a partially hydrogenated oil (mixture of partially hydrogenated soybean oil and palm oil). The authors concluded that the partially hydrogenated oil (mixture of hydrogenated soybean oil and palm oil) contained a low quantity of conjugated linoleic acid isomers (4.24 mg total CLA/g oil).

Jung and Ha (1999) reported conjugated linoleic acid formation in vegetable oils during selective and nonselective hydrogenation processes. The large quantity of conjugated linoleic acids in soybean oil was formed during selective hydrogenation processes. The conjugated linoleic acid content in hydrogenated soybean oil obtained from the hydrogenation at the temperature of 215 °C and hydrogen pressure of 7.1 psi was 98 mg/g oil, which was one of the highest ever reported in foods (Jung and Ha 1999). However, the authors reported that maximum contents of conjugated linoleic acids in hydrogenated soybean oil obtained by conventional hydrogenation with nonselective nickel catalyst at the temperature of 215 °C and hydrogen pressure of 35.5 psi was 9.06 mg/g oil. Jung and Jung (2002) separated methyl esters of conjugated linoleic acids in hydrogenated soybean oil by a silver-ion ( $\text{Ag}^+$ ) impregnated high-pressure liquid chromatography and identified the methylated conjugated linoleic acids by gas chromatography-mass spectrometry. The gas chromatogram and identification of methyl esters of conjugated linoleic acids is shown in Figure 4. The silver ion-impregnated high-pressure liquid chromatography and identification of conjugated linoleic acid methyl

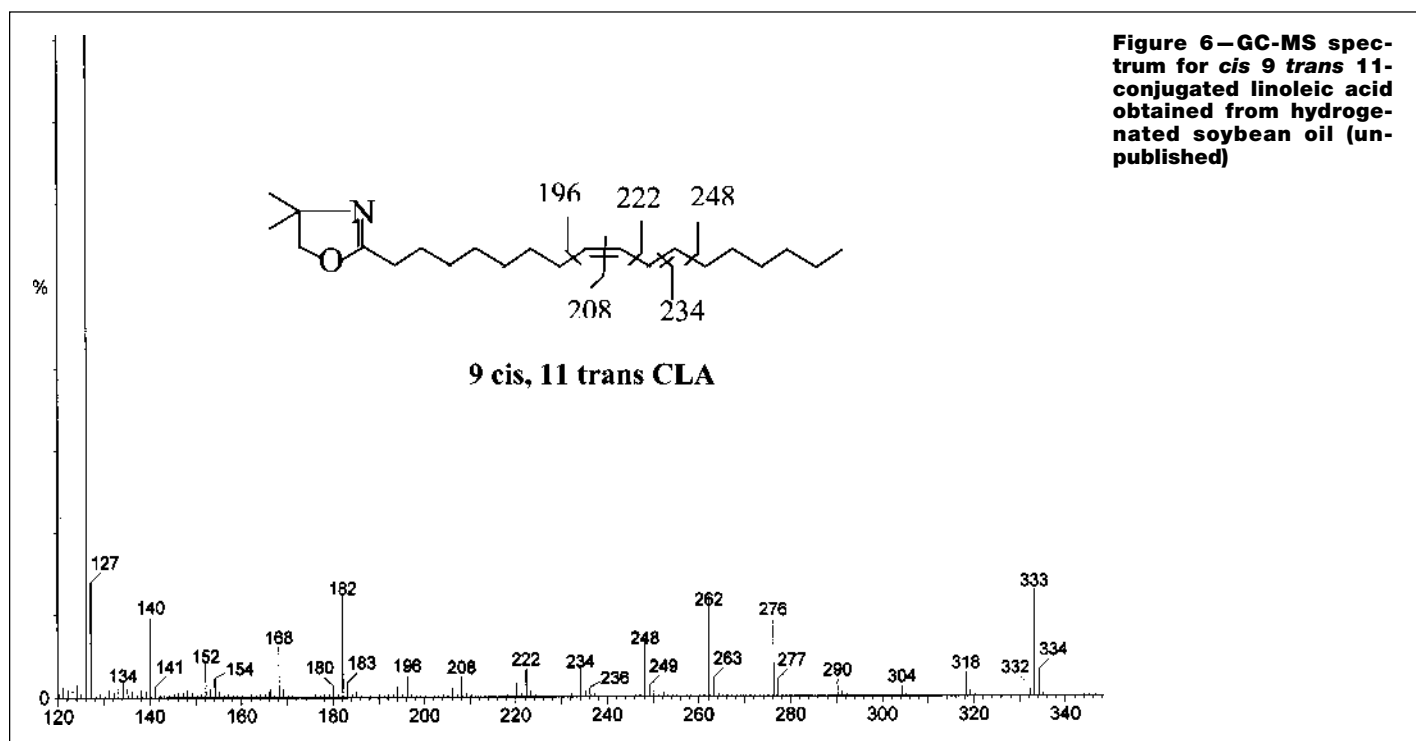


esters of hydrogenated soybean oil are shown in Figure 5. Jung and Jung (2002) separated conjugated linoleic acids of hydrogenated soybean oil by using a silver ion-impregnated high-pressure liquid chromatography and identified 22 methylated conjugated linoleic acids of soybean oil by gas chromatography-mass spectrometry. Figure 6 shows gas chromatography-mass spectrometry spectrum for *c9t11* conjugate linoleic acid obtained from hydrogenated soybean oil. The best-known CLA isomers are the *c9t11* and *t10c12* isomers. However, other CLA isomers of *trans, trans*- or *cis, cis*- are shown to have biological activities in the previously reported paper (Bulgarella and others 2001). Bulgarella and others (2001) reported that the inhibition efficacy of prostaglandin H synthesis activity, which is involved in tumor growth in numerous systems, followed by *t10c12*-, *t9t11*-, *c9c11* isomers, in decreasing order.

Various hydrogenation conditions are applied to produce hydrogenated oils with different physical and chemical properties whenever needed. The hydrogenation conditions greatly affect the types of fatty acids in hydrogenated vegetable oils. Jung and others (2001, 2002) reported the effects of catalyst types, catalyst amount, reaction temperature, agitation rate, hydrogen pressure, and different oils on the quality and quantity of conjugated linoleic acids of hydrogenated soybean oil with a selective Ni catalyst. The selective Ni catalysts produced higher conjugated linoleic acids in soybean oil than the nonselective type Ni catalysts. As the catalyst content increased, the conjugated linoleic acids content of hydrogenated soybean oil increased. As the hydrogen pressure increased, the conjugated linoleic acids content in soybean oil decreased. The higher the temperature and the lower the agitation rate of the reactor were, the higher the conjugated linoleic acids content in the hydrogenated soybean oil was. Jung and others (2001, 2002) concluded that the gas-liquid mass transfer limitation conditions of low hydrogen pressure, low stirring rate, high catalyst content, and high reaction temperature favored the production of conjugated linoleic acids in vegetable oils during hydrogenation. The stirring rate and reaction temperature have most



**Figure 5—Silver ion-impregnated high-pressure liquid chromatogram of methylated conjugated fatty acids of hydrogenated soybean oil. *trans* 13,*trans* 15- (peak 1), *trans* 12, *trans* 14- (peak 2), *trans* 11, *trans* 13- (peak 3), *trans* 10, *trans* 12- (peak 4), *trans* 9, *trans* 11- (peak 5), *trans* 8, *trans* 10- (peak 6), *trans* 7, *trans* 9- (peak 7) /*trans* 12,*cis* 14- (peak 8); *cis* 12,*trans* 14- (peak 9); *trans* 11,*cis* 13- (peak 10) *cis* 11,*trans* 13- (peak 11); *cis* 10,*trans* 12- / *trans* 10,*cis* 12- (peak 12); *cis* 9, *trans* 11-/*trans* 9,*cis* 11- (peak 13); *trans* 8,*cis* 10-/*cis* 8, *trans* 10- (peak 14), *cis* 10,*cis* 12- (peak 15); *cis* 9,*cis* 11- (peak 16), *cis* 8,*cis* 10- (peak 17). (Adapted from Jung and others 2002)**



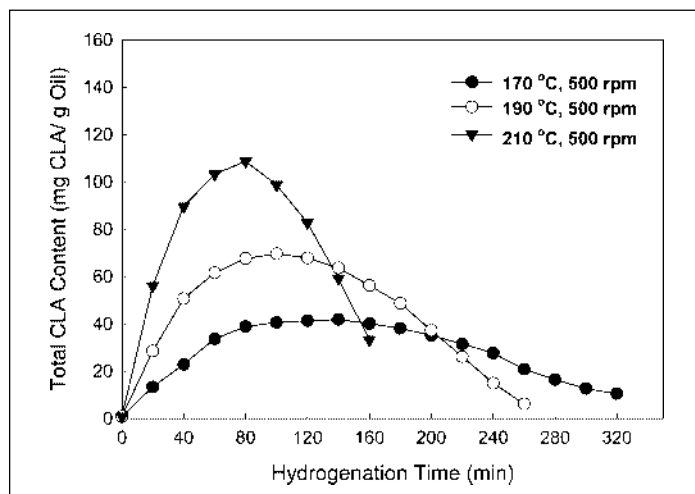
**Figure 6—GC-MS spectrum for *cis* 9 *trans* 11-conjugated linoleic acid obtained from hydrogenated soybean oil (unpublished)**

significant effects on the formation of conjugated linoleic acids in soybean oil during hydrogenation among the hydrogenation conditions. Figure 7 and 8 show the effects of temperature and stirring rate on the contents of conjugated linoleic acids of soybean oil during hydrogenation, respectively. The contents of conjugated linoleic acids in hydrogenated corn oil, cottonseed oil, or soybean oil under the mass transfer limited condition reached 250 mg/g oils (Figure 9). These oils also contained relatively high quantity (about 8% to 10%) of *trans* C<sub>18:1</sub> isomers, which are known to be associated with an increased risk of cardiovascular disease. But Jung and others (2002) reported that mild hydrogenation (10 min) with selective type nickel catalyst at low hydrogen pressure (7.11 psi) and high temperature (230 °C) produced oils containing high amount of CLA (48.16mg CLA/g oil), which was about 8 times greater than levels in major dietary sources for CLA, such as dairy products and ruminant meat. The authors reported that obtained oil contained only 3.5% *trans* fatty acids. Choi and others (2004) studied the effects of selectively hydrogenated soybean oil with

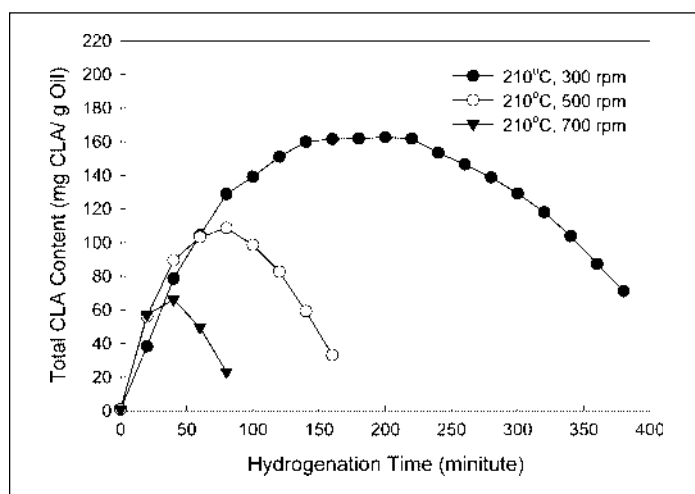
high CLA on body composition and plasma lipid in rats. The authors reported that 5% dietary supplementation of the selectively hydrogenated soybean oil with high CLA induced the reductions of 23.3% body fat and 44.3% of total cholesterol.

The selective nickel with sulfur produced high conjugated linoleic acids in hydrogenated vegetable oils. Ju and Jung (2003) hypothesized that the poisoning effect of sulfur might be responsible for the promotion of conjugated linoleic acid formation during hydrogenation. The qualitative and quantitative effects of sulfur addition on the formation of conjugated linoleic acids in vegetable oils during hydrogenation with nonselective type Ni catalyst showed that sulfur addition greatly increased the conjugated linoleic acids of hydrogenated soybean oil. As the amount of sulfur increased to a certain level, the conjugated linoleic acids in soybean oil increased greatly during hydrogenation. However, the higher sulfur above the optimum level decreased the conjugated linoleic acids formation. Ju and Jung (2003) reported that during hydrogenation with 0.1% nickel, the maximum contents of CLA formed with 0, 20, 40, 60, 80, and 100 ppm sulfur additions were 40.8, 126.3, 158.3, 171.9, 160.3, and 152.5 mg of CLA/g oil, respectively. The optimal sulfur level for the promotion of conjugated linoleic acids formation changed with the amount of nickel used. The optimal ratio of sulfur to nickel for the increase of conjugated linoleic acids formation was always 0.06:1, regardless of the nickel amount used. At the 0.06:1 ratio of sulfur to nickel, the higher the nickel content was, the higher the conjugated linoleic acids content in the hydrogenated soybean oil was. The increase of nickel from 0.05% to 0.15% at the optimal sulfur to nickel ratio increased the conjugated linoleic acids content by 50%. The conjugated linoleic acids compositions were greatly affected by both sulfur addition and amounts of nickel.

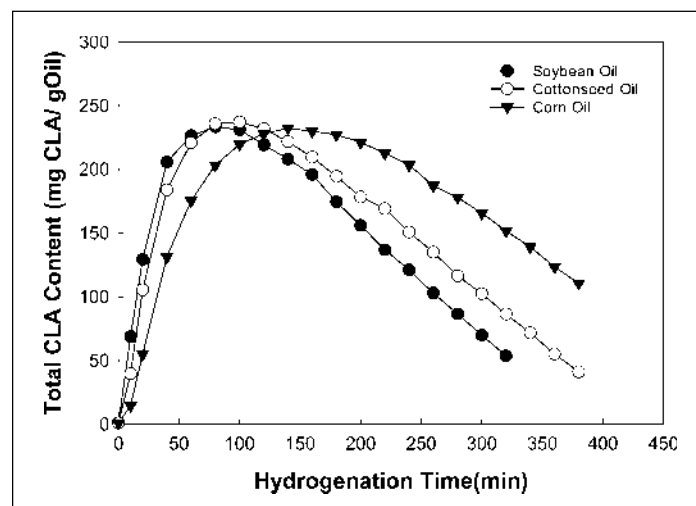
Ju and others (2003) studied the effects of catalytic transfer hydrogenation with alcohol as a hydrogen source on the formation of conjugated linoleic acids. Catalytic transfer hydrogenation has been introduced as an alternative method for classical hydrogenation of edible oils and fats. The classical hydrogenation techniques use molecular hydrogen gas, but the catalytic transfer hydrogenation uses alcohols and organic acids as hydrogen donors for hydrogen source (Mondal and Lalvani 2000; Naglic and others 1998; Basu and Chakrabarty 1966; Chakrabarty and others 1972; Arkad and others 1987; Tagawa and others 1978). One of



**Figure 7—Effects of hydrogenation temperatures on the conjugated linoleic acids of soybean oil with selective type nickel catalyst, hydrogen pressure 7 psi, and agitation rate 500 rpm. (Adapted from Jung and others 2001)**



**Figure 8—Effects of stirring rate on the conjugated linoleic acids of soybean oil with selective type nickel catalyst, hydrogen pressure 7 psi, and temperature 210 °C. (Adapted from Jung and others 2001)**



**Figure 9—Effects of hydrogenation temperature on the conjugated linoleic acids of soybean oil, canola oil, and cottonseed oil during hydrogenation with selective nickel catalysts at 230 °C, hydrogen pressure 7 psi, and stirring rate of 180 rpm. (Adapted from Jung and others 2002)**



the major advantages of the catalytic transfer hydrogenation is to use safe hydrogen donors as an alternative for dangerous gaseous hydrogen. The generalized Eq. 8 represents this process.



where D, H, and A represent hydrogen donor, hydrogen, and hydrogen acceptor, respectively.

Ju and others (2003) reported that butanol and propanol showed the highest activity for the formation of conjugated linoleic acids, followed by ethanol and methanol. As the amount of alcohol in the reaction system increased from 0% to 2.5%, the conjugated linoleic acids formation increased greatly. However, the conjugated linoleic acids formation decreased above 2.5% ethanol. The authors reported that the CLA contents in the hydrogenated soybean oil with 0%, 0.5%, 1.0%, 2.5%, 5.0%, 10.0%, and 15.0% ethanol for 150 min were 0.8, 69.6, 91.2, 120.4, 108.7, 87.3, and 61.2 mg/g oil. Hydrogenation time and alcohol content also greatly influenced the isomeric distribution of conjugated linoleic acids in soybean oils. The higher the alcohol contents and the longer the hydrogenation time induced the greater distribution of *trans trans* CLA isomers in the oil. Ju and others (2003) claimed that the catalytic transfer hydrogenation with alcohol has a distinct advantage over the classical hydrogenation with molecular hydrogen gas in producing hydrogenated soybean oil with high concentration of conjugated linoleic acids.

## Conclusions

Health concerns about *trans* fatty acids formed by hydrogenation have led to the use of interesterification, fractionation, or blending of saturated and polyunsaturated oils as an alternate method to hydrogenation. These alternatives are costly and do not easily produce the desirable physical and chemical properties of oils suitable for the broad ranges of food products. Therefore, the alternate methods could not easily replace the hydrogenation of vegetable oils. Hydrogenation is still the viable choice for food manufacture if *trans* fatty acids can be substantially reduced during the hydrogenation processes. New hydrogenation processes such as electrocatalytic hydrogenation, precious catalyst hydrogenation, and supercritical fluid state hydrogenation have shown promising results for the reduction of *trans* fatty acids below the level of 8%. These hydrogenation techniques would be viable alternatives for replacing the conventional Ni catalyst hydrogenation to produce the hydrogenated products with low *trans* fatty acids. However, further research should be followed on economic feasibilities of new hydrogenations and reusability of precious metal catalysts. Hydrogenation with selective type Ni catalyst under the mass transfer limitation conditions of high catalyst content, low stirring rate, high temperature, and low hydrogen pressure showed the high quantity of conjugated linoleic acids (as high as 240 mg/g oil) formation in vegetable oils. Mild hydrogenation (10 min) with selective type nickel catalyst at low hydrogen pressure (7.11 psi) and high temperature (230 °C) produced oils containing high amount of CLA (48.16 mg CLA/g oil) and low level of *trans* fatty acids (3.5%). The CLA amount of 48.16 mg/g oil was about 8 times greater than levels in major dietary sources for CLA, such as dairy products and ruminant meat. The hydrogenated vegetable oils with high quantity conjugated linoleic acid might provide the possibility for the utilization of hydrogenated oils as health-promoting food ingredients.

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