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Studies in catalytic transfer hydrogenation of soybean oil using ammonium formate as donor over 5% Pd/C catalyst

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Abstract

The catalytic transfer hydrogenation (CTH) is a novel, alternative process for the selective hydrogenation of soybean oil due to the lower rate of formation of stearic acid and *trans*-isomer, which have an adverse health effects. Ruthenium and palladium supported catalysts were screened along with hydrogen donors during CTH process. The CTH of soybean oil was studied using aqueous ammonium formate solution over supported palladium catalyst. The method offered good selectivity in complete reduction of linolenic acid with a slight increase in stearic acid. The kinetics of CTH of soybean oil using ammonium formate as a hydrogen donor over 5% Pd/C catalyst was studied. The speed of agitation was sufficiently high enough to eliminate diffusional resistance. The CTH of soybean oil was described by pseudo-first order kinetic model. Runge–Kutta algorithm (RKS4) was used to determine the kinetic rate constants. The catalyst could be reused thrice without any adverse effect.

Keywords: Ammonium formate; Catalytic transfer hydrogenation; Soybean oil; Linolenic; Palladium

1. Introduction

Soybean oil consists of mainly triglycerides of saturated and unsaturated fatty acids, particularly with a C_{16}–C_{18} chain length. Hydrogenation of soybean oil is an important process in oleochemical industry because of its wide applications to produce margarine, frying oils, etc. The general purpose of this unit process is to increase the melting point, improve color and oxidation properties of the liquid oil. The selective reduction of linolenic acid ($C_{18:3}$) in soybean oil has a prime importance to alter flavor reversion of the oil. The quality and physical properties of the final product during hydrogenation are greatly affected by the number of double bonds present in the oil, i.e. the iodine value (IV) and the *cis*–*trans*-isomers of fatty acid. The *trans*-isomer has been reported to be undesirable for human diet due to adverse health effects [1].

Copper-chromite is universally employed, commercial catalyst for the selective hydrogenation of soybean oil. Though the copper-chromite is most selective for hydrogenating the linolenic acid in soybean oil and other vegetable oils, drawback of commercially available copper-chromite catalysts is that they are much less active at low hydrogen pressures, in fact this catalyst required high temperature and high pressure condition [2,3]. Copper-chromite formed the highest amount of *trans*-isomers than palladium and nickel catalyst. Copper-chromite catalyst poses spent catalyst disposal problems due to Cr content. Commercially employed Ni catalysts have a limited linolenic selectivity. Consequently, soybean oil hydrogenated to an iodine value (IV) of 110 still contains 3% linolenic acid [4].

The catalytic transfer hydrogenation (CTH) is a promising alternative technique in order to study selective hydrogenation of edible oils [5–7]. This process allows control over the formation of stearic acid effectively. The CTH is a safe, simple and eco-friendly method, compared to the conventional catalytic hydrogenation, in which hydrogen gas is replaced with a hydrogen donor. The compounds used as hydrogen donors are easy to store, handle, and transport, unlike pure hydrogen gas under pressure. The CTH technique does not require high-pressure operation and elaborate precautionary method, used in conventional catalytic hydrogenation. The CTH provides an effective manufacturing tool to small or medium scale manufacturers who do not have experience and system dealing with high-pressure hydrogenation.

The commonly used hydrogen donors are cyclohexene, cyclohexadiene, phosphinic acid, hydrazine, formic acid, sodium formate, ammonium formate and sodium hypophos-

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Nomenclature

A	linolenic ($C_{18:3}$) acid
B	linoleic ($C_{18:2}$) acid
C	oleic ($C_{18:1}$) acid
(C_A)	concentration of linolenic acid (wt.%)
(C_B)	concentration of linoleic acid (wt.%)
(C_C)	concentration of oleic acid (wt.%)
(C_D)	concentration of stearic acid (wt.%)
D	stearic ($C_{18:0}$) acid
(D_H)	hydrogen donor concentration (kmol/m^3)
IV	iodine value (g iodine/100 g soybean oil)
k_{IV}	overall pseudo-rate constant for unsaturation (min^{-1})
k^*_{IV}	intrinsic rate constant for unsaturation (min^{-1})(kmol/m^3)$^{-1}$(kg cat/kg oil)$^{-1}$
k_x	rate constant of the reaction step x in series (min^{-1})
k^*_x	intrinsic rate constant of the reaction step x in series (min^{-1})(kg cat/kg oil)$^{-1}$(kmol/m^3)$^{-1}$
r	overall rate of reaction (−d(IV)/dt)
r_0	initial rate (−d(IV)/dt at $t = 0$)
R_1	carbon chain bonded to triglycerides
R_2	terminal carbon chain
S_I	linolenic selectivity (k_1/k_2)
S_{II}	linoleic selectivity (k_2/k_3)
t	reaction time (min)
w	concentration of the catalyst in % (w/w) of oil (kg cat/kg oil)
x	subscript of the rate constant indicating the reaction step in series (i.e. 1, 2, 3)

phite [8]. Basu and Chakrabarty [9] and Chakrabarty et al. [10] showed that secondary alcohols also could be used as hydrogen donors, but only under relatively extreme conditions with a reduced selectivity. Arkad et al. [5] have studied CTH of soybean oil methyl esters in a concentrated aqueous alkali formate solution at 80 °C and reported almost complete hydrogenation after 16 h of reaction. Smidovnik et al. [11] carried out CTH of soybean oil with various formic acid salts as hydrogen donors in organic and aqueous media. In organic media the linoleic acid content could not be reduced below 13.1%, with essentially no changes in the content of stearic acid after 24 h, whereas in aqueous medium the linoleic acid content decreased to 1.4% and stearic acid increased from 5.4% to 10.8% after 33 h of reaction time. Smidovnik et al. [6,12] also studied the kinetics of CTH of soybean oil and reported the reduction of only linolenic acid up to 1% with a relatively high level of linoleic acid without much increase in stearic acid concentration using sodium formate as a donor. Naglic et al. [7,13] studied the CTH of vegetable oils and soybean lecithin in an aqueous sodium formate solution by using 10% Pd/C and observed that stearic acid content increases. Arkad et al. [5] reported that formates are superior to other hydrogen donors. They are very reactive donors and side reactions, liberation of gaseous hydrogen is relatively slow compared to the other donors. Thereby offering intrinsic safety. However, very little information is available for the CTH of soybean oil using aqueous ammonium formate solution over 5% Pd/C catalyst.

In present work, selective reduction of linolenic acid ($C_{18:3}$) in soybean oil was attempted using a CTH technique without any additive to enhance the mass transfer process in this heterogeneous system. The additive has to be food grade for edible oil application. Ammonium formate was preferred as hydrogen donor because it decomposes into H_2, CO_2 and ammonia after the reaction, which can be easily washed out with water whereas the sodium formate donors leaves Na_2CO_3 residues as the reaction products in aqueous phase. The gaseous ammonia evolved can be absorbed in formic acid and ammonium formate thus formed could be recycled back thereby conserving ammonia. Only very small quantities of ammonia loss via hydrogen generation needs to be replaced. The hydrogen evolved due to side reaction is too small to cause alarming safety concerns. Therefore, a systematic study of catalytic transfer hydrogenation (CTH) of soybean oil was undertaken using aqueous ammonium formate as hydrogen donor and palladium on carbon as the catalyst to aid development of the CTH process.

2. Experimental

2.1. Materials

The refined soybean oil, supplied by M/s Godrej Industries Ltd., Mumbai, India was used for hydrogenation as such. The fatty acid composition and properties of refined soybean oil used is given in Table 1. Palladium chloride and ruthenium trichloride trihydrate (pure), used as the catalyst precursor, were obtained from SISCO Research Laboratories Pvt. Ltd., Mumbai, India. Alumina support was obtained from Degussa, Germany. Carbon support was procured from s.d. fine chemicals, Mumbai, India. The hydrogen donors (ammonium formate, potassium formate and sodium formate) were purchased from s.d. fine chemicals, Mumbai, India. All chemicals and solvents for product analy-

Table 1
Fatty acid composition and properties of refined soybean oil

Fatty acid composition and properties	Values
%Fatty acid composition	
C12:0	0.2
C14:0	0.4
C16:0	11.8
C18:0	4.3
C18:1	22.4
C18:2	54.0
C18:3	5.6
C20:0	0.5
C22:0	0.4
C24:0	0.4
Iodine value (Wijj's)	132.2
Acid value	0.2
Average molecular weight (based on fatty acid compositions)	871.4

sis were of high purity, and used as such without any further processing.

2.2. Catalyst preparation: formaldehyde reduction

In order to prepare the 5% Pd/C catalyst, an aqueous solution of palladium chloride ($PdCl_2$) in deionised water (hydrochloric acid was used to dissolve $PdCl_2$) was rapidly contacted with the finely divided support (activated carbon support which was pretreated with HNO_3 at 80 °C for 2 h followed by washing and drying) and the slurry was stirred for 2 h at 30 °C and kept overnight. The slurry was then contacted with sodium hydroxide solution to precipitate palladium as a hydroxide. It was stirred again and heated at 60 °C for 1 h. After settling, the top aqueous layer was separated from the precipitate below. Deionised water was then added to the precipitate and this solution was then allowed to digest at 80 °C for an hour. Excess formaldehyde and an additional amount of the precipitant were then added to the mixture to ensure the completion of reduction, and heating at 80 °C was continued for another hour. This was followed by cooling, filtration, washing and drying. A silver nitrate solution was used to ascertain the absence of Cl^- ions. Smaller sized catalyst particles were obtained by sieving through the appropriate mesh size. The 5% Ru/C and 5% Pd/Al_2O_3 catalysts were prepared in similar fashion with the respective metal precursors added in appropriate amounts. The BET surface areas of the catalysts were determined using a Micromeritics ASAP 2010 analyzer by nitrogen adsorption. The particle size ranges were determined by using a particle size analyzer (Coulter LS 230). The scanning electron micrographs (model JSM 6380 LA of JEOL Ltd., Japan) of 5% Pd/C catalyst and carbon support are depicted in Fig. 1(a and b).

2.3. Experimental setup

The schematic diagram of the experimental setup is shown in Fig. 2. The catalytic transfer hydrogenation of soybean oil was studied in 250 cm^3 capacity, mechanically agitated glass reactor, having 6.5 cm i.d. The glass reactor was equipped with six blade impeller (diameter, 2.5 cm; width, 8 mm), four baffles and thermo well for measuring reaction mixture temperature. A reflux condenser with provision for chilled water as a coolant was also mounted on the reactor. The entire setup was immersed in a constant temperature water bath. The temperature in the water bath was maintained with temperature indicator and controller (TIC) within ±1 °C of the set temperature.

2.4. Experimental procedure

Weighed amounts of oil, donor solution (aqueous) were taken in a glass reactor. The reactor was immersed in a thermostatically controlled water bath with mechanical stirring. Catalyst was added after the desired temperature reach. The progress of the hydrogenation reaction was monitored by determining the iodine value (IV) and fatty acid composition of samples removed periodically during the process.

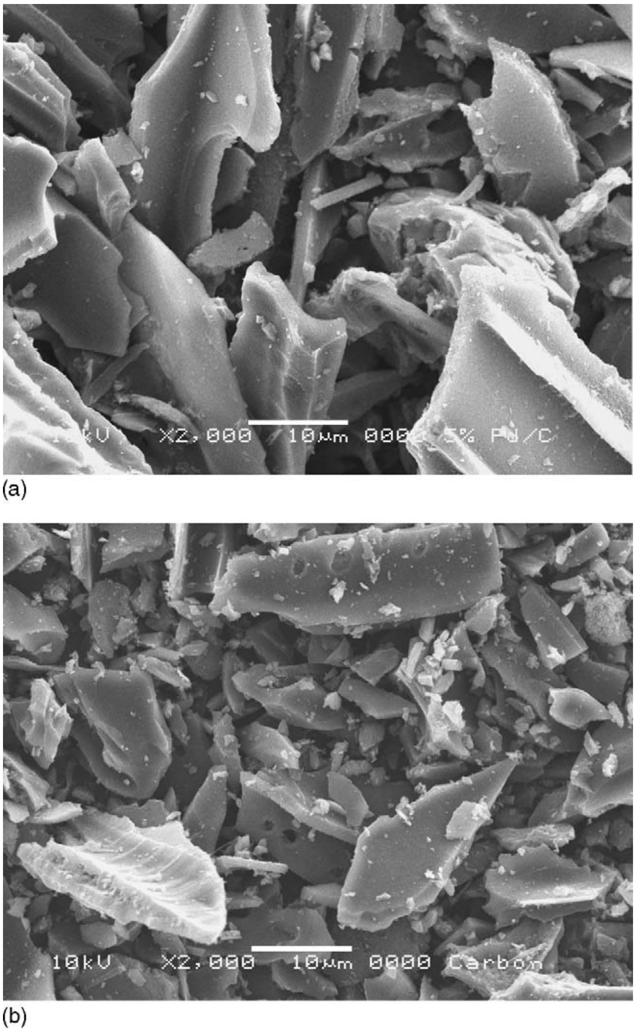

Fig. 1. Scanning electron micrograph of (a) 5% Pd/C catalyst and (b) carbon support.

2.5. Product analysis

Samples were withdrawn at various time intervals during hydrogenation. Sample contain oil phase (which included the catalyst) was diluted with *n*-hexane and separated from the aqueous phase. After filtering of the catalyst, the *n*-hexane was evaporated and the reaction products were analyzed by Wijj's method [14] to find iodine value (IV), which determine the degree of unsaturation. For quantitative analysis, methyl esters were prepared from hydrogenated soybean oil with sodium methoxide catalyst and gas chromatographically analyzed using BPX-70 (70% cyanopropyl polysilphenylene–siloxane) capillary column (30 m × 0.32 mm i.d.) mounted on gas chromatograph (model Chemito 1000, Chemito Technologies Pvt. ltd., Mumbai, India) with a flame ionization detector (FID). The column was operated at 120–230 °C with 3 °C/min rate with hydrogen as carrier gas. Injector ports and detector were held at 250 and 260 °C, respectively. This analysis allowed to determined quantitatively all kinds of fatty acid methyl esters and geometrical *cis–trans*-isomers. There was a very good match between the iodine value

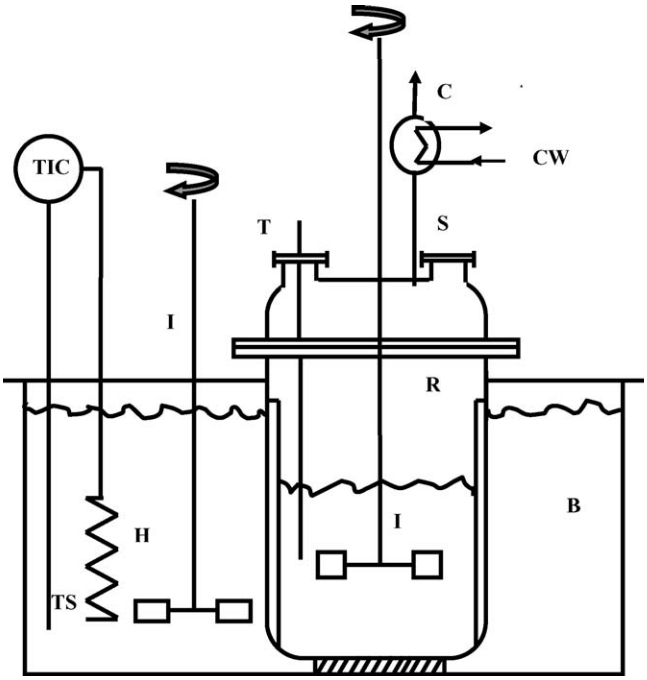

Fig. 2. Experimental setup for catalytic transfer hydrogenation (CTH) of soybean oil. B, constant temperature water bath; H, heater; TS, temperature sensor; R, glass reactor; TIC, temperature indicator and controller; I, impeller; S, sampling port; T, thermo well; C, condenser; CW, chilled water.

(IV) obtained from Wijj's method and that estimated from gas chromatograph technique.

3. Results and discussion

The overall mechanistic insight into catalytic transfer hydrogenation (CTH) using ammonium formate as hydrogen donor can be presented as:

- main reaction:

$$HCOONH_4 \rightleftarrows NH_4^+ + HCOO^- \tag{1}$$

$$HCOO^- + H_2O + Pd \rightleftarrows H\text{–}Pd\text{–}H + HCO_3^- \tag{2}$$

$$H\text{–}Pd\text{–}H + R_1\text{–}CH{=}CH\text{–}R_2 \rightarrow R_1\text{–}CH_2\text{–}CH_2\text{–}R_2 + Pd \tag{3}$$

$$HCO_3^- \rightleftarrows OH^- + CO_2\uparrow \tag{4}$$

$$NH_4^+ + OH^- \rightarrow NH_3\uparrow + H_2O \tag{5}$$

$$HCOONH_4 + R_1\text{–}CH{=}CH\text{–}R_2 \rightarrow R_1\text{–}CH_2\text{–}CH_2\text{–}R_2 + NH_3\uparrow + CO_2\uparrow \tag{6}$$

- side reaction:

$$H\text{–}Pd\text{–}H \leftrightarrows Pd + H_2\uparrow \tag{7}$$

The primary objective of present work is to study selective hydrogenation of soybean oil using a novel CTH process. The desired specifications of hydrogenated product are: the contents of linolenic acid be less than 1% with relatively more linoleic acid and without much increase in stearic acid. Catalytic transfer hydrogenation of soybean oil was studied using aqueous ammonium formate solution and a palladium on carbon catalyst. The effects of various parameters such as speed of agitation, type of the catalyst, type of hydrogen donor, reaction temperature, donor concentration, reactant concentration, quantity of water, soybean oil concentration and catalyst loading were studied. We shall deal them one by one.

3.1. Mass transfer considerations

The catalytic transfer hydrogenation (CTH) process studied was a heterogeneous system involving two immiscible liquids namely soybean oil and aqueous ammonium formate solution and the solid catalyst, 5% Pd/C. The diffusional process (mass transfer) of oil and formate getting transported to active catalyst center depends upon the intensity of turbulence in the liquid phase. For a given reactor geometry and type of an impeller, the rotational speed (rpm) decides the intensity of turbulence. In order to study the effect of agitation, experiments were conducted at 90 °C. It was observed that the reduction in IV increased with an increasing speed of stirring upto 600 rpm. Above this value the reduction in IV was independent of stirring speed. This effect was quantified in terms of the dependence of initial rate on the speed of stirring as depicted in Fig. 3. All experiments were, therefore, conducted at 1000 rpm, wherein inter particle mass transfer resistance was eliminated. The absence of intraparticle mass transfer resistance was confirmed by studying the effect of catalyst particle size on the rate of CTH hydrogenation. In order to ascertain the absence of pore diffusion, experiments were also performed with two particle sizes in the ranges 45–63 to 75–90 μm (sieve method) at 90 °C. It was observed that the catalyst particle size had no effect on the rate of reaction, and hence, pore diffusion was deemed to be absent.

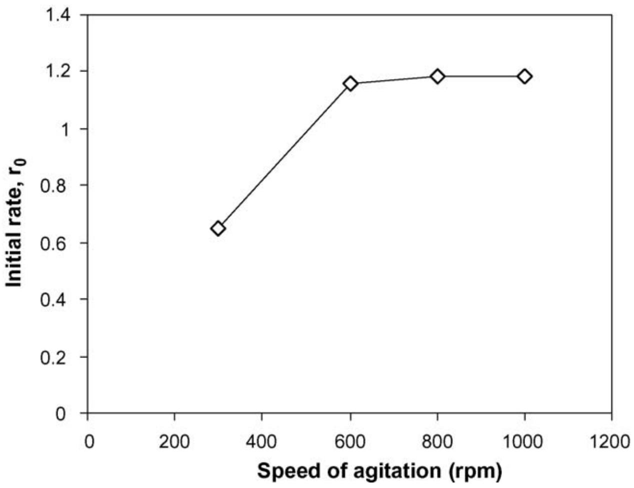

Fig. 3. Effect of speed of agitation on initial rate (90 °C, donor concentration 4.4 kmol/m^3 (0.32 mol/50 ml H_2O), catalyst loading 2% (w/w) of soybean oil, soybean oil 0.012 mol).

Table 2
Characteristics of the various heterogeneous catalysts

Catalysts	Property and values				
	BET surface area ($m^2 g^{-1}$)	Micropore volume ($cm^3 g^{-1}$)	Average pore diameter (Å)	Particle size range (μm)	Mean diameter (μm)
5% Pd/C	1098	0.37	20.4	6–25	19
5% Ru/C	1085	0.39	22.7	10–30	22
5% Pd/Al_2O_3	102	0.027	153	43–69	54

Thus, under the experimental conditions employed, all diffusional resistances (intra particle and inter particle) have been eliminated and hence it was possible to discern true kinetics from the experimental observations.

3.2. Catalyst screening

The interactions of support with the active catalytic phase can influence the activity and selectivity of the catalyst. The main characteristics of 5% Pd/C, 5% Ru/C and 5% Pd/Al_2O_3 catalysts are depicted in Table 2. The characteristics of 5% Pd/C and 5% Ru/C catalysts have no significant difference. Although carbon support has significant effect on catalyst performance, active metal decides the activity of catalyst. It is seen that the catalyst Pd on alumina exhibited lower BET surface area, which in turn affects the catalyst activity. The performance of these catalysts on the course of CTH hydrogenation was studied. The catalytic activity for catalytic transfer hydrogenation of refined soybean oil in the aqueous ammonium formate solution was studied using various catalysts at temperature 90 °C and at catalyst loading 2% (w/w) of soybean oil. The hydrogenation activity was monitored by the reduction in iodine value (IV). The catalytic transfer hydrogenation activity on 5% Ru/C and 5% Pd/Al_2O_3 was found to be very less than that of 5% Pd/C. The catalyst support interaction is obvious from Fig. 4. The effect of concentration of Pd on carbon support was studied at 90 °C using ammonium formate as an active hydrogen donor. It was observed that with 1% Pd/C catalyst reaction proceed very slowly. However, with an increasing the concentration of Pd on carbon support reaction rate increased. The catalyst 1% Pd/C exhibited very poor activity as compared to 5% Pd/C catalyst. Therefore, 5% Pd/C was used as a potential catalyst for selective reduction of linolenic acid in soybean oil using CTH process. This catalyst is also commercially readily available. The SEM images of 5% Pd/C catalyst and carbon support are depicted in Fig. 1(a and b). The SEM images shows that catalyst and support particles are irregular in shape. It is seen that the catalyst preparation procedure (impregnation technique) leads to the formation of catalyst with slight change in morphology resulting in slightly larger particles, as depicted in SEM images in Fig. 1(a and b). This can be attributed to catalyst preparation method. Recently, Gabrovska et al. [15] have also observed change in morphology of the support during preparation of Ni based catalyst for hydrogenation of edible oil.

3.3. Donor

Effect of type of donor on CTH of soybean oil was studied. Experiments were conducted at reaction temperature 90 °C with 4.4 M aqueous donor concentration. It was observed that ammonium formate exhibited better activity under the conditions employed during the catalytic transfer hydrogenation (Fig. 5). In case of sodium and potassium formate reaction proceed slowly as compared to ammonium formate this might be due to formation of alkali salts in the reaction mixture (Na_2CO_3,

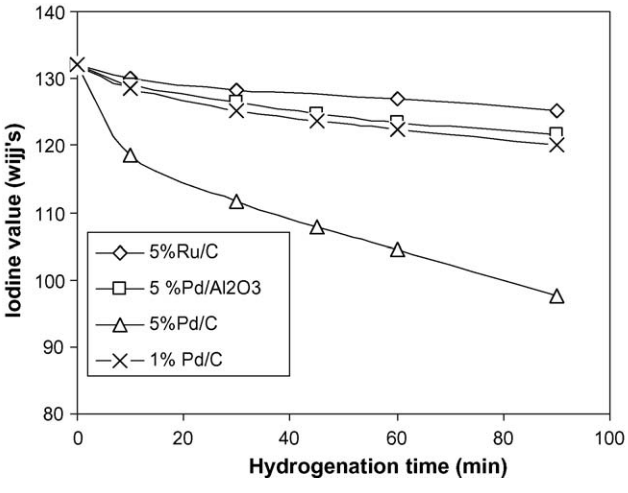

Fig. 4. Effect of various type of catalyst on reduction in IV during CTH of soybean oil (90 °C, donor concentration 4.4 $kmol/m^3$ (0.32 mol/50 ml H_2O), catalyst loading 2% (w/w) of soybean oil, soybean oil 0.012 mol).

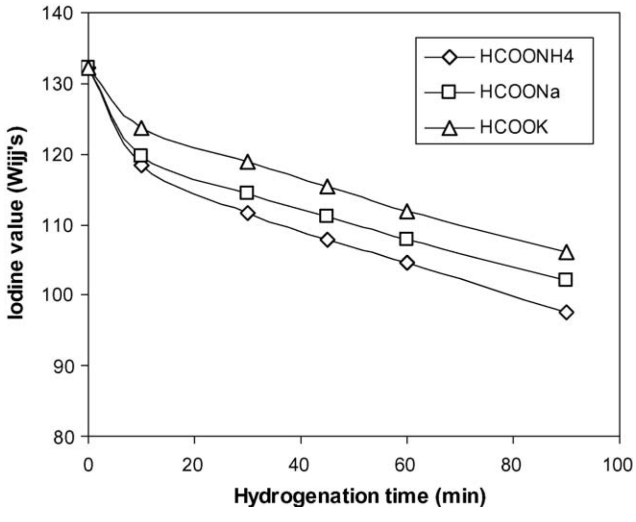

Fig. 5. Effect of type of donor on reduction in IV during CTH of soybean oil (90 °C, donor concentration 4.4 $kmol/m^3$ (0.32 mol/50 ml H_2O), catalyst loading 2% (w/w) of soybean oil, soybean oil 0.012 mol).

K_2CO_3, $NaHCO_3$, $KHCO_3$), which might have affected adsorption of reactant and palladium hydride formation on the active centers. The detailed studies related to this aspect have been excluded from the scope of this investigation. Ammonium formate will result in ammonia which can be when desorbed from the solution could be easily absorbed in formic acid thereby producing ammonium formate. In the case Na or K formate, the aqueous solution will contain respective carbonates. This carbonate when neutralized to adjust acidic pH for the waste treatment by Fenton reagent ($FeSO_4$, H_2SO_4, and H_2O_2) would release CO_2, causing frothing in the system which is highly undesirable. Thus while selecting a donor one has to consider recovery of the cationic species (Na^+, K^+, NH_4^+) as well as the ease of the waste treatment. Based on this integrated approach we decided to use ammonium formate as hydrogen donor in further studies presented.

3.4. Process parameters

In order to get better insight into CTH process, various process parameters studied over 5% Pd/C as the catalyst, are discussed below.

3.4.1. Donor concentration

The ammonium formate concentration determines the activity of both formate and water. Water also participates stoichiometrically in the reaction as seen from Eq. (2) in the above mechanistic insight. Effect of donor concentration was studied by varying the concentration from 2.3 to 4.4 M at 90 °C with catalyst loading 2% (w/w) of soybean oil. Fig. 6 exhibits the reduction in iodine value (IV) with different initial donor concentration. It was observed that hydrogenation was more efficient at and above 4.2 M aqueous ammonium formate solution. However, at 2.3 M aqueous ammonium formate solution, which is stoichiometrically desired amount resulted slower rate of reaction with no *trans*-isomers. Further excess amount of donor helped to complete reduction of linolenic acid with slightly increase in stearic concentration. Excess amount of ammonium formate was needed, since some of the formate decomposes, yielding hydrogen, which was lost, and because the concentration of formate decreased as the reaction proceeded, resulting in reduced hydrogenation rate. All experiments were conducted at 4.4 M aqueous ammonium formate concentration. Thus, effect of donor concentration was eliminated.

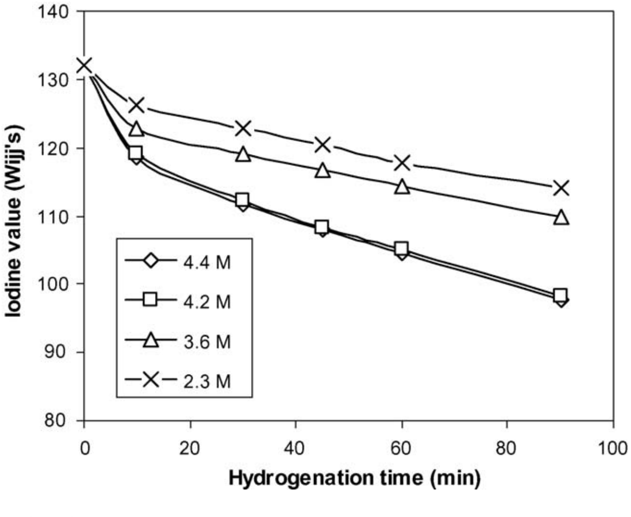

Fig. 6. Effect of ammonium formate donor concentration on reduction in IV during CTH of soybean oil (90 °C, 50 ml H_2O, catalyst loading 2% (w/w) of soybean oil, soybean oil 0.012 mol).

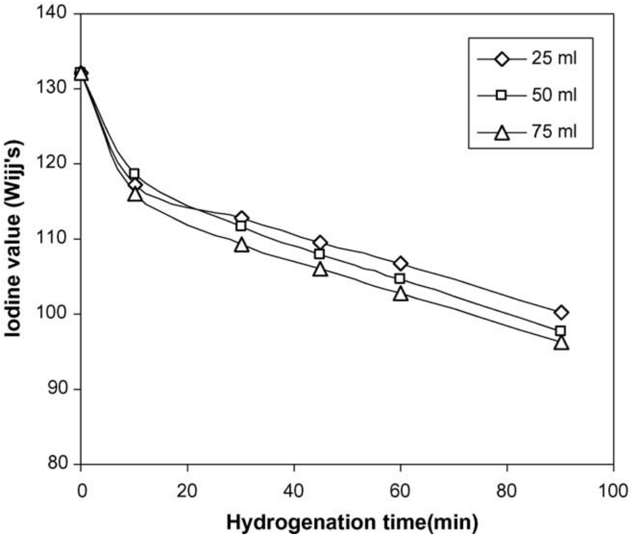

Fig. 7. Effect of amount of water on reduction in IV during CTH of soybean oil (90 °C, donor 0.32 mol, catalyst loading 2% (w/w) of soybean oil, soybean oil 0.012 mol).

After eliminating the effect of donor concentration, the effect of water was studied. It is seen from the above Eq. (2) not only formate but also water plays a role by abstracting CO_2 as HCO_3^-. Fig. 7 shows the effect of water where the ammonium formate is diluted by varying quantity of water from 25 to 75 cm^3, in which the donor is still in great excess in relation to the desired product. Further, it seems that increasing dilution of formate solution resulted in faster reduction in unsaturation than higher concentration of donor solution 6.8 M. Higher concentrations slows down the reaction. This happens probably because the reaction proceeds through competitive adsorption of water and formate to active sites on the catalyst surface [16]. Fig. 8 shows the dependency of donor concentration towards the initial rate. It was observed that initial rate increased with an increasing donor concentration. However, at 3.2 M aqueous ammonium formate solution initial rate was the highest, further increase in donor concentration resulted in the reduction in the rate. Though the rate was highest in case of 3.2 M aqueous ammonium formate solution, it was observed that formation of stearic acid in soybean oil also increased with lower linoleic selectivity under the condition employed during CTH process. Beyond the concentration of donor 4.2 M, there was no effect on the initial rate (Fig. 8). Therefore, the donor concentration in aqueous solution was kept 4.4 M for further studies. This behavior could be attributed to difference in adsorption behavior of various components on the active center. We have excluded from the scope of this work the detail study pertaining to adsorption.

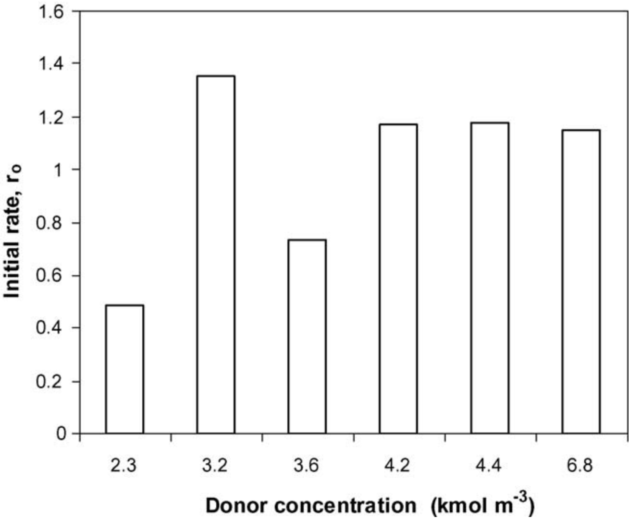

Fig. 8. Effect of donor concentration on initial rates during CTH of soybean oil (90 °C, catalyst loading 2% (w/w) of soybean oil, soybean oil 0.012 mol [donor concentration: 2.3 M (0.14 mol/50 ml H_2O); 3.2 M (0.32 mol/75 ml H_2O); 3.6 M (0.24 mol/50 ml H_2O); 4.2 M (0.30 mol/50 ml H_2O); 4.4 M (0.32 mol/50 ml H_2O); 6.8 M (0.32 mol/25 ml H_2O)]).

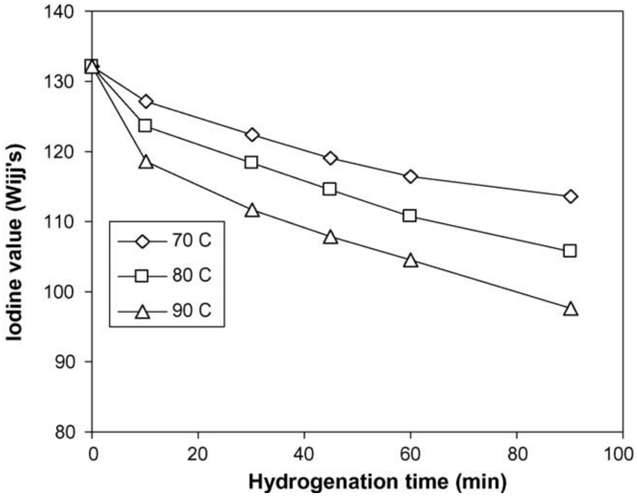

Fig. 10. Effect of reaction temperature on reduction in IV during CTH of soybean oil (donor concentration 4.4 M (0.32 mol/50 ml H_2O), catalyst loading 2% (w/w) of soybean oil, soybean oil 0.012 mol).

3.4.2. *Catalyst loading*

The effect of catalyst loading was studied at temperature 90 °C and 4.4 M aqueous ammonium formate solution. The catalyst loading has profound effect on reduction in IV during hydrogenation in the range of 1–4% (w/w) of soybean oil. The initial rate was found to vary linearly with the various catalyst loading in the above range studied (Fig. 9).

3.4.3. *Reaction temperature*

In order to study the effect of temperature some experiments were conducted in the temperature range from 70 to 90 °C with aqueous donor concentration 4.4 M at speed of agitation 1000 rpm. The catalyst loading was 2% (w/w) of soybean oil. It was observed that temperature has pronounced effect on the CTH of soybean oil. Fig. 10 shows that reduction in IV increased with an increase in reaction temperature. Concentration profiles obtained from GC technique showed that formation of stearic acid ($C_{18:0}$) increased with an increase in reaction temperature but this increase in $C_{18:0}$ is not much (say $C_{18:0} \leq 7.2\%$). Fig. 13 depicts the concentration profiles obtained at 90 °C during CTH of soybean oil.

3.4.4. *Concentration of soybean oil*

During the hydrogenation reaction, unsaturated fatty acids compete with the hydrogen donors through adsorption at the active sites on the catalyst surface where they are gradually converted to the saturated product. In order to study the effect of reactant concentration experiments were conducted at 90 °C with 4.4 M aqueous donor concentration by varying soybean oil concentration from 0.012 to 0.024 mol in reaction mixture with constant catalyst loading. Fig. 11 shows the reduction in

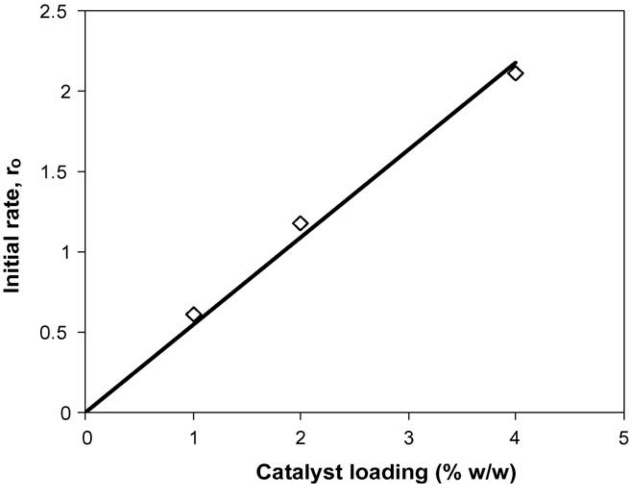

Fig. 9. Effect of catalyst loading on initial rates during CTH of soybean oil (90 °C, donor concentration 4.4 M (0.32 mol/50 ml H_2O), soybean oil 0.012 mol).

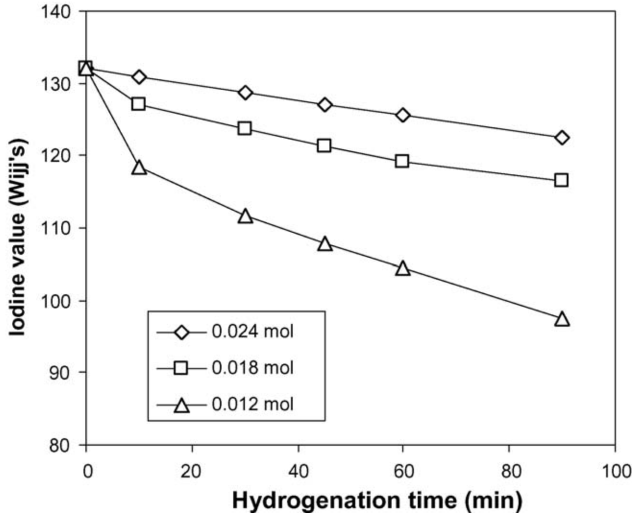

Fig. 11. Effect of soybean oil concentration on reduction in IV during CTH of soybean oil (90 °C, donor concentration 4.4 M (0.32 mol/50 ml H_2O), catalyst 0.2 g).

IV decreased with an increasing soybean oil concentration. It was observed that at 0.024 mol soybean oil the rate of reaction proceeds very slowly. However, at 0.012 mol soybean oil reaction proceeds faster with desired product specifications (Fig. 13). Concentration profiles obtained from GC technique shows that the linolenic acid ($C_{18:3}$) and linoleic acid ($C_{18:2}$) concentration decreased with time, and only a small amount of stearic acid ($C_{18:0}$) was formed until the linolenic almost totally disappeared. Further linoleic acid ($C_{18:2}$) slowly disappeared with increasing concentration of oleic acid ($C_{18:1}$), while stearic acid ($C_{18:0}$) was not much increased.

4. Kinetic model

4.1. Rate expression in terms of IV

In order to facilitate process design attempts were made to develop kinetic rate expressions for this CTH reaction at 4.4 M aqueous ammonium formate concentration. It is well known that the saturation of double bonds follows a first order simple kinetics with respect to reduction of IV. Thus, dependence between rate and reactant concentration in terms of IV can be expressed as:

$$r = -\frac{\mathrm{d(IV)}}{\mathrm{d}t} = k_{\mathrm{IV}}(\mathrm{IV}) \tag{8}$$

The above expression was valid at excess donor concentration (ammonium formate). Thus at constant donor concentration (excess) dependency of donor was imbedded in the rate constant as:

$$k_{\mathrm{IV}} = k^{*}_{\mathrm{IV}}(D_{\mathrm{H}})(w) \tag{9}$$

The value of k_{IV} was evaluated at different temperatures (70, 80 and 90 °C), using the integral method. Thus the value of rate constant at 70, 80 and 90 °C were found to be 0.0017, 0.0028 and 0.0039 min^{-1}, respectively, under the conditions employed during hydrogenation. From the temperature dependence of the reaction rate constant, the energy of activation was found to be 43.1 kJ/mol (Fig. 12). This clearly indicates that reaction is in kinetically controlled regime under the conditions employed during hydrogenation. The simple rate expression (8) above is very important for designing commercial reactor.

4.2. Rate expression in terms of fatty acids concentration

In order to have even a better insight into selective hydrogenation of soybean oil, it was thought desirable to find the rate expression in terms of fatty acid concentrations at 4.4 M aqueous ammonium formate concentration. Hydrogenation of soybean oil is a complex chemical reactions involving hydro isomerisation. The various reactants compete with each other for catalyst active sites. Soybean oil contained saturated and unsaturated fatty acid particularly C_{18} chain length. During the hydrogenation reaction fatty acid compete with hydrogen donors through adsorption for the active sites on the catalyst surface where they are gradually converted to the saturated state. Thus the elimination of polyunsaturated fatty acid and the formation of monounsaturated fatty acid can be described with consecutive reaction.

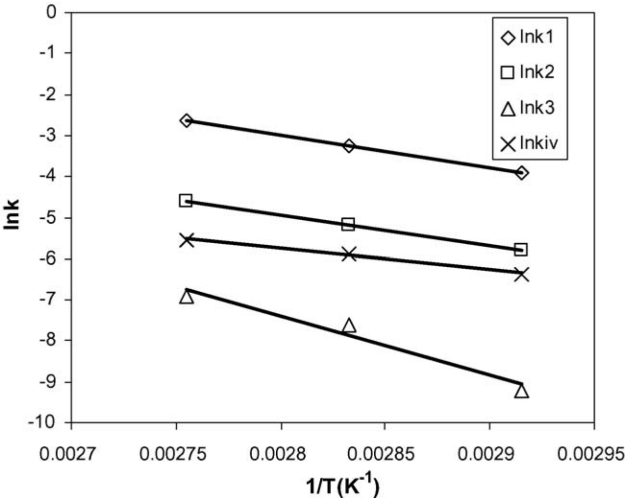

Fig. 12. Temperature dependence of the reaction rate constant (70–90 °C, donor concentration 4.4 M (0.32 mol/50 ml H_2O), catalyst loading 2% (w/w) of soybean oil, soybean oil 0.012 mol).

For a kinetic description of such a system, *cis–trans* compositions are lumped together. Therefore, now hydrogenation reaction can be represented as a series reaction:

$$\underset{(C_{18:3})}{\mathrm{A}} \xrightarrow{k_1} \underset{(C_{18:2})}{\mathrm{B}} \xrightarrow{k_2} \underset{(C_{18:1})}{\mathrm{C}} \xrightarrow{k_3} \underset{(C_{18:0})}{\mathrm{D}} \tag{10}$$

To illustrate the procedure describing the overall hydrogenation pseudo-kinetics, all reactions were considered to be irreversible and first order with respect to substrate. Moreover, in the experimental CTH conditions used in this work, the reactant hydrogen donor was in excess of stoichiometric quantity required. Its concentration (D_{H}) is considered to be constant over the duration of the hydrogenation process at constant catalyst concentration. Therefore, this concentration is imbedded in the rate constant k_x as:

$$k_x = k^{*}_{x}(D_{\mathrm{H}})(w) \tag{11}$$

With these simplification and assumptions, the rates of reactions depicted in Eq. (10) can be expressed as:

$$-\frac{\mathrm{d}(C_{\mathrm{A}})}{\mathrm{d}t} = k_1(C_{\mathrm{A}}) \tag{12}$$

$$\frac{\mathrm{d}(C_{\mathrm{B}})}{\mathrm{d}t} = k_1(C_{\mathrm{A}}) - k_2(C_{\mathrm{B}}) \tag{13}$$

$$\frac{\mathrm{d}(C_{\mathrm{C}})}{\mathrm{d}t} = k_2(C_{\mathrm{B}}) - k_3(C_{\mathrm{C}}) \tag{14}$$

$$\frac{\mathrm{d}(C_{\mathrm{D}})}{\mathrm{d}t} = k_3(C_{\mathrm{C}}) \tag{15}$$

where $(C_{\mathrm{A}}) = (C_{\mathrm{A}})_0$, $(C_{\mathrm{B}}) = (C_{\mathrm{B}})_0$, $(C_{\mathrm{C}}) = (C_{\mathrm{C}})_0$ and $(C_{\mathrm{D}}) = (C_{\mathrm{D}})_0$ at $t = 0$.

The unknown parameters k_1, k_2, k_3 can be identified from above equations by the least-square technique with combination of Runge–Kutta algorithm (RKS4).

Table 3
Rate parameters with standard deviation, correlation coefficient and RSS for kinetic model (Eqs. (12)–(15))

Temperature (°C)	Standard deviation			Correlation coefficient, r^2	RSS
	k_1 (min^{-1})	k_2 (min^{-1})	k_3 (min^{-1})		
70	$0.020 \pm 1.0 \times 10^{-3}$	$0.0030 \pm 1.0 \times 10^{-4}$	$0.0001 \pm 2.0 \times 10^{-6}$	0.99	16.3
80	$0.038 \pm 1.2 \times 10^{-3}$	$0.0055 \pm 3.7 \times 10^{-4}$	$0.0005 \pm 2.9 \times 10^{-5}$	0.99	24.3
90	$0.072 \pm 5.0 \times 10^{-3}$	$0.0100 \pm 7.0 \times 10^{-4}$	$0.0010 \pm 3.6 \times 10^{-5}$	0.98	35.2

The parameter estimation was performed for all experiments at different temperature. The residual sum of square (RSS) was minimized by a simplex algorithm, least square technique.

The RSS of rate parameters at different temperature are given in Table 3. The RSS represents the sums of the squares of the difference between the experimental and predicted composition of fatty acid profile of soybean oil. The values of k_1, k_2, k_3 obtained at different temperature with standard deviation and correlation coefficient are also shown in Table 3.

The rate constants obtained from kinetic model shows that rate of hydrogenation of oleic acid is much slower than the linolenic and linoleic acid. From the temperature dependence of the reaction rate constant, the energy of activation was found to be 66.1 kJ/mol for linolenic acid, 62.3 kJ/mol for linoleic acid and 120 kJ/mol for oleic acid (Fig. 12). This clearly indicates that reaction in series is in kinetically controlled regime under the conditions employed during present hydrogenation studies. These values match reasonably well with those reported in case of CTH of soybean oil using sodium formate as donor [6,12].

4.2.1. Validation of the model

The validation of the kinetic model was performed by simultaneously solving and non-linearly fitting these differential equations with experimental data. Typical results of predicted profiles of fatty acids along with those experimentally obtained with 5% Pd/C catalyst are shown in Fig. 13. As seen, good agreement was found between the experimental and the predicted values, as described by kinetic model.

4.3. Selectivity towards desired product

In vegetable oil hydrogenation, the notation of selectivity is important. Present work deals that hydrogenated product should contain less than 1% linolenic ($C_{18:3}$) without substantially increase in stearic acid ($C_{18:0}$). In order to monitor adequately hydrogenation towards the desired products, it is useful to introduce selectivities. A well-known and accepted method to determine the selectivity is from the ratio of reaction rate constants [17] governing the reaction as shown in Eq. (10). The concept of “traditional” selectivity, as introduced by Coenen [18] describing the preference for hydrogenation of polyenes rather than monoenes is estimated by the ratio of rate constant. Thus:

$$S_{\mathrm{I}} = \frac{k_1}{k_2} \tag{16}$$

$$S_{\mathrm{II}} = \frac{k_2}{k_3} \tag{17}$$

where S_{I} and S_{II} represents the linolenic and linoleic selectivity, respectively.

High values of S_{II} mean that the rate at which $C_{18:1}$ (oleic acid) produced from more unsaturated fatty acid is greater than the rate at which $C_{18:1}$ itself is hydrogenated to stearic acid. For industrial hardening, this selectivity is the most important parameter and hydrogenation is considered to be selective when S_{II} is higher than 10 [19], and at very low value of S_{II} (<5) stearic acid formation start from the beginning of reaction, whereas at high value of S_{II} its formation is held back until the linoleic acid is almost eliminated [20]. The various selectivities computed as above under the conditions employed during CTH process are presented in Table 4.

The rate constant k_1, k_2, k_3 for linolenic, linoleic and oleic acid, respectively, were found to decrease during CTH of soybean oil, which indicates that single double bonds are poorly hydrogenated than two and three double bonds. The rate constant for oleic acid was very low which indicates the formation of stearic acid was substantially very low. The value of rate constant obtained at different temperature increased with an increasing reaction temperature (Table 4) and linolenic selectivity increases slightly, i.e. rate of disappearance of linolenic increases with an increasing temperature, whereas linoleic selectivity decreases with an increasing reaction temperature which indicates the formation of oleic acid increases with an increasing temperature with small amount of stearic acid formation.

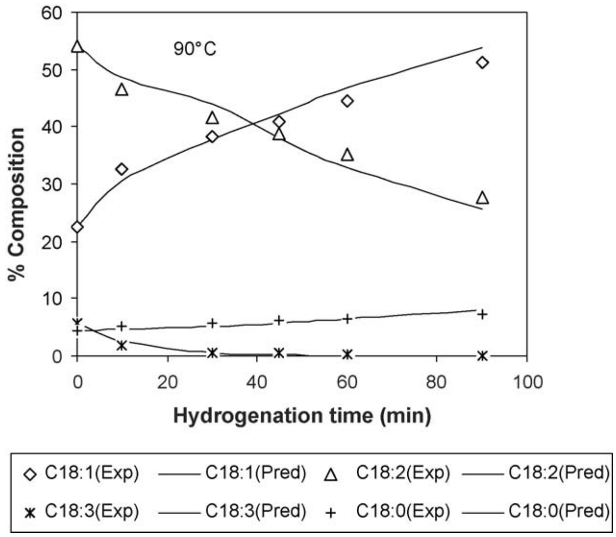

Fig. 13. Comparison of predicted values of % composition of fatty acids in soybean oil with experimental values (90 °C, donor concentration 4.4 M (0.32 mol/50 ml H_2O), catalyst loading 2% (w/w) of soybean oil, soybean oil 0.012 mol).

Table 4
Effect of various process parameters on linolenic and linoleic selectivity during CTH of soybean oil

Donor	Temperature (°C)	Concentration of donor (kmol m^{-3})	Catalyst loading, % (w/w)	k_1 (min^{-1})	k_2 (min^{-1})	k_3 (min^{-1})	Linolenic selectivity (k_1/k_2)	Linoleic selectivity (k_2/k_3)
NH_4OOCH	70	4.4	2	0.020	0.0030	0.00010	6.7	30.0
	80	4.4	2	0.038	0.0055	0.00050	6.9	11.0
	90	4.4	2	0.072	0.0100	0.00100	7.2	10.0
	90	4.4	1	0.032	0.0041	0.00050	7.8	8.2
	90	4.4	4	0.120	0.0180	0.00130	6.6	13.9
	90	2.3	2	0.018	0.0029	0.00032	5.8	9.0
	90	3.2	2	0.080	0.0120	0.00130	6.7	9.2
	90	3.6	2	0.041	0.0065	0.00070	6.3	9.3
	90	6.8	2	0.058	0.0080	0.00089	7.3	9.0
NaOOCH	90	4.4	2	0.060	0.0082	0.0012	7.3	6.8
KOOCH	90	4.4	2	0.054	0.007	0.0014	7.7	5.0

Donor concentration: 2.3 M (0.14 mol/50 ml H_2O); 3.2 M (0.32 mol/75 ml H_2O); 3.6 M (0.24 mol/50 ml H_2O); 4.4 M (0.32 mol/50 ml H_2O); 6.8 M (0.32 mol/25 ml H_2O).

It was observed that the rate of reaction increased with an increasing catalyst loading. Further, it was observed that linolenic selectivity decreased, i.e. rate of disappearance of both linolenic and linoleic acid increases rapidly whereas linoleic selectivity increased with an increasing catalyst loading which indicates the rate of disappearance of linoleic increases rapidly with formation of oleic acid and small amount of stearic acid. Thus, the rate of reduction of linoleic acid was faster with increasing formation of oleic acid at higher catalyst loading after complete reduction of linolenic acid. However, at limited amount of catalyst, content of both linolenic and linoleic acid decreased slowly. The value of selectivities obtained at various donor concentration (2.3–6.8 M) was shown in Table 4. The value of selectivities obtained for CTH of soybean oil using sodium and potassium formate donors were also shown in Table 4.

5. Reusability of the catalyst

In order to study the reusability of this catalyst, three experiments were conducted on fresh solution of reaction mixture with same catalyst reused after separation from the solution by filtration. The results showed that the activity of the catalyst remained more or less the same after three recycles.

6. Hydrogenation process comparison

It was thought desirable to compare catalytic hydrogenation with H_2 gas and the catalytic transfer hydrogenation (CTH) process. It is desired that *trans*-isomer formation be minimum. Therefore, an attention was focussed on this issue while comparing two processes. For hydrogenation of soybean oil using hydrogen gas in high pressure and high temperature, experiments were conducted in SS 316 Parr high-pressure reactor of capacity 300 cm^3. The solvent used was *n*-dodecane using commercial Ni (Nysosel-222) and 5% Pd/C catalyst in presence of 2% (w/w) water. Thus, experiments were conducted at temperature 150 °C and H_2 pressure 0.68 MPa with catalyst loading 0.4% (w/w) of soybean oil. Meanwhile, CTH of soybean oil was conducted in 250 cm^3 glass reactor at 90 °C and 4.4 M hydrogen donor with catalyst loading 2% (w/w) of soybean oil. Effect of this study was shown in Table 5. Comparison of commercial hydrogenation process with present CTH process was done at desired specification of hydrogenated product. It was observed that CTH process gave lower *trans*-isomer. It is well known that formation of *trans*-isomer increases with increase in temperature. Consequently, the CTH process was found to be quite good as it offered selective hydrogenation with lower *trans*-isomer.

Table 5
Effect of hydrogenation process on the formation of *trans*-isomers (geometrical) during soybean oil hydrogenation

Hydrogenation process	Time (min)	IV (Wijj's)	%Composition of fatty acids (fatty acid methyl esters)						%Reduction in IV
			$C_{18:0}$	$C_{18:1}$		$C_{18:2}$		$C_{18:3}$	
				Cis	*Trans*	*Cis*	*Trans*		
–	0	132.2	4.3	22.4	0	54.0	0	5.6	–
CTH (5% Pd/C; 90 °C)	30	111.2	5.7	38.3	0	41.2	0.5	0.6	15.9
High-pressure (Ni; 150 °C)	20	110.7	7.5	37.6	0	37.3	2.0	1.9	16.2
High-pressure (5% Pd/C; 150 °C)	5	110.3	7.2	37.4	0	37.6	3.6	0.52	16.5

CTH: 90 °C, donor concentration 4.4 M (0.32 mol/50 ml H_2O), catalyst loading 2% (w/w) of soybean oil, soybean oil 0.012 mol, speed of agitation 1000 rpm. High-pressure: 150 °C, 0.68 MPa H_2 pressure, catalyst loading 0.4% (w/w) of soybean oil, soybean oil 0.16 kmol/m^3 (*n*-dodecane as a solvent), water 2% (w/w), speed of agitation 1200 rpm.

7. Environmental aspects

In the present work, CTH process of soybean oil contains aqueous ammonium formate solution with very high COD (about 2,00,000 mg/L). Therefore, it was thought desirable to study wastewater treatment of this aqueous stream before disposal. In order to study treatment of aqueous waste of the CTH process, Fenton technique [21] was used to reduce COD (chemical oxygen demand) and TOC (total organic carbon). This technique uses hydrogen peroxide and an iron catalyst to reduce COD and TOC of wastewater. One exploratory experiment was conducted under acidic pH (say 2) at 30 °C with iron catalyst (Fe^{2+}) using hydrogen peroxide as oxidant (Fenton chemistry). It was observed that COD and TOC of aqueous ammonium formate solution reduced effectively (75%). The detailed studies related to Fenton's technique have been excluded from the scope of this investigation.

8. Conclusion

A novel, alternative hydrogenation process (CTH) was used for the selective hydrogenation of linolenic acid in soybean oil using aqueous ammonium formate solution and a palladium on carbon catalyst. The 5% Pd/C was found to be a suitable catalyst for the CTH of soybean oil. The CTH process for soybean oil allows control over the formation of stearic acid effectively. The method offered good selectivity in complete reduction of linolenic acid with a slight increase in stearic acid. Formation of *trans*-isomers was found to be lower during CTH of soybean oil than hydrogenation using hydrogen molecule under high pressure.

The experimental data were well described with pseudo-first order kinetic model. The kinetic rate constants and selectivity was determined under intense speed of agitation. The catalyst activity remained constant even after three recycles.

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