

Research Article

Hydrogenation of Some Vegetable Oils by Scrap Automobile Catalyst

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Some vegetable oils were hydrogenated with scrap automobile catalyst (SAC) as a catalyst. The optimum reaction conditions (solvent, reaction time, and catalyst amount) were determined. Our results showed that the linoleic acid was reduced to elaidic acid in the sunflower oil. This procedure not only gives high yields but also allows recycling of automobile wastes as a catalyst in organic reactions and is representative of green chemistry.

1. Introduction

Hydrogenation of fats and oils is a very important operation in the industrial process of producing vegetable tallow, vegetable fats, margarines, and starting components for the cosmetic and chemical industry such as emulsifiers, soaps, creams, pastes, and similar substances [1]. There are two main reasons why hydrogenation is important to the industry. The first is increasing the stability of the oil. Highly unsaturated oil is susceptible to autoxidation, thermal decomposition, and other reactions that affect the flavor. Consequently, it is desired to partially hydrogenate the oil to improve shelf life. The second reason to partially hydrogenate vegetable oil is to improve its utility. For most products, such as shortenings, margarines, or confectionery fats, the desired softening and melting characteristics correspond to oils that are partially hydrogenated. The choice of catalyst to use for hydrogenation greatly affects the properties of the final product [2].

Several catalysts for hydrogenation of oils are known in the literature, such as Rh/TPPTS complexes [3], Cu/SiO₂ [4], Ni/SiO₂ [5] and Pd/SiO₂ [6–8] catalysts, Ni/Ru mixture [9], and Ni/Al₂O₃ catalyst [10].

In continuation of our studies on the development of novel heterogeneous synthetic methodologies [11–14], we have achieved a novel procedure for the hydrogenation of sunflower oils catalyzed by scrap automobile catalyst (SAC)

which was used for the hydrogenation of carbon-carbon double bonds in our previous study [15].

The lifetime of catalytic converters is limited and thus their recycling is crucial. Catalytic converters consist of a ceramic substrate coated with aluminum oxide (Al₂O₃) and other rare earth oxides, such as CeO₂, ZrO₂, Pt, Pd, and Rh which are responsible for the catalytic function [16]. A used automobile catalytic converter was taken from a Fiat Siena after running for 140,000 km. After purification of the SAC, it was activated in an oven maintained at 120°C for 12 h and found to contain 0.465% Pd and 0.040% Rh by XRF analysis.

2. Experimental Procedures

2.1. General. ¹H and ¹³C NMR spectra were measured on spectrometer at VARIAN Infinity Plus 300 and at 75 Hz, respectively. ¹H and ¹³C chemical shifts are referenced to the internal deuterated solvent. Solvents were dried following standard methods. All chemicals were purchased from Merck, Alfa Easer, Sigma-Aldrich, and Fluka and the oils were purchased from local supermarket.

2.2. Purification of the Catalyst. A piece of scrap catalyst (50 g) cut by hacksaw was taken from the automobile catalytic converter and washed with chromic acid and distilled water

TABLE 1: Catalytic hydrogenation of some vegetable oils using SAC.

Oil type	Time (h)	Amount of oil (g)	Amount of catalyst (g)	Solvent	Iodine value
Sunflower oil	—	4	—	—	117.00
	48	4	1	THF	112.55
	48	4	2	THF	88.88
	48	4	3	THF	42.70
	48	4	4	THF	23.68
	6	4	4	THF	54.01
	12	4	4	THF	53.71
	18	4	4	THF	45.47
	24	4	4	THF	39.70
	30	4	4	THF	36.63
	36	4	4	THF	34.44
	42	4	4	THF	30.69
	72	4	4	THF	22.77
	48	4	4	Diethyl ether	32.71
	48	4	4	Hexane	44.18
	48	4	4	Acetone	35.73
48	4	4	Isopropanol	34.48	
Hazelnut oil	—	4	—	—	89.96
	48	4	4	THF	30.38
Tea seed oil	—	4	—	—	57.52
	48	4	4	THF	20.96

to remove dust and carbonaceous particles. The scrap catalyst was dried in an oven maintained at 120°C for 12 h, crushed in agate mortar and sieved (<100 μm in diameter), and analyzed by XRF.

2.3. Optimization of Reaction Conditions. To optimize the hydrogenation reaction, we examined the reaction conditions in different solvents, such as THF, diethyl ether, hexane, isopropanol, and acetone, for the different reaction times (6 h, 12 h, 18 h, 24 h, 30 h, 36 h, 42 h, 48 h, and 72 h) and different amount of catalyst (1 g, 2 g, 3 g, and 4 g). We determined optimization by low iodine value. Thus, the best results were obtained in THF for 48 h with 4 g catalyst (Table 1).

2.4. Hydrogenation Procedures. A solution of the sunflower oil (4.0 g) in anhydrous THF (25 mL) was transferred into a two-neck round bottom flask containing the purified catalyst (4 g). Reactions were carried out by stirring under atmospheric pressure of H_2 at room temperature for 48 h. The reaction mixture was filtered and the filtrate was evaporated under vacuum.

2.5. Iodine Value. Iodine values of the partially hydrogenated oils were determined by the known procedures [17].

3. Results and Discussion

To optimize study of this hydrogenation reaction, the solvent effect of these liquid phase hydrogenation reactions depended on the solubility and chemisorption of H_2 and

on the catalyst suspended in the solvent. The solubility and chemisorption of H_2 in a nonpolar solvent are greater than in polar solvents [18]. Also, rising reaction times and amount of catalyst increased the amount of hydrogenated oils. After 48 hours, rising the hydrogenation was quite sluggish (Table 1). So, the optimum reaction time was considered 48 hours.

The ^1H and ^{13}C NMR spectra of oils have been reported in the literature [19–21]. The ^1H NMR spectra of sunflower oil, which contains linoleic acid (58%), oleic acid (31%), stearic acid, and palmitic acid (11%), show signals between 5.30 and 5.40 ppm relating to olefinic protons of all acyl chains, at 2.75 ppm for bisallylic protons and at 2.04 ppm for allylic protons of linoleyl chains (Figure 1(a)). On the other hand, the signals of bisallylic protons and allylic protons of linoleyl chains cannot be seen at the ^1H NMR spectra of hydrogenated sunflower oil (Figure 1(b)) and it shows that the intensity of signals of the olefinic protons decreased. Although the signals of C9-10 and C12-13 carbons of linoleic acid can be seen between 128.1 and 130.3 ppm at the ^{13}C NMR spectra of sunflower oil (Figure 2(a)), they cannot be seen at ^{13}C NMR spectra of hydrogenated sunflower oil (Figure 2(b)). Additionally, the ^{13}C NMR spectra of hydrogenated sunflower oil showed a chemical shift for the *trans*-allylic carbons at 32.8 ppm but no chemical shift at 27.3 ppm [22], confirming that no *cis*-isomers were present in this product. Based on these results, the linoleic acid was hydrogenated to elaidic acid in the sunflower oil. These results are consistent with declining iodine value and confirm the hydrogenation of sunflower oil.

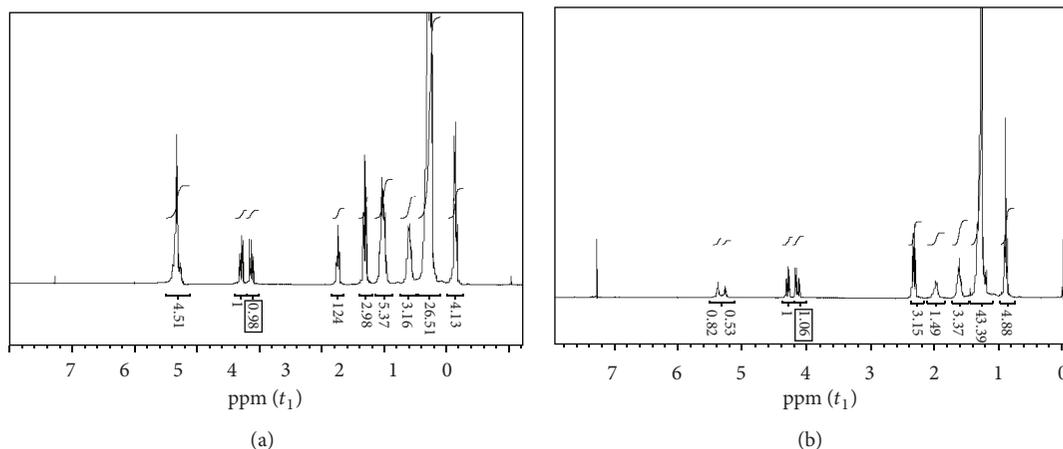


FIGURE 1: Comparison of the 300 MHz ^1H -NMR spectra of sunflower oil (a) and hydrogenated sunflower oil (b) in CDCl_3 solutions.

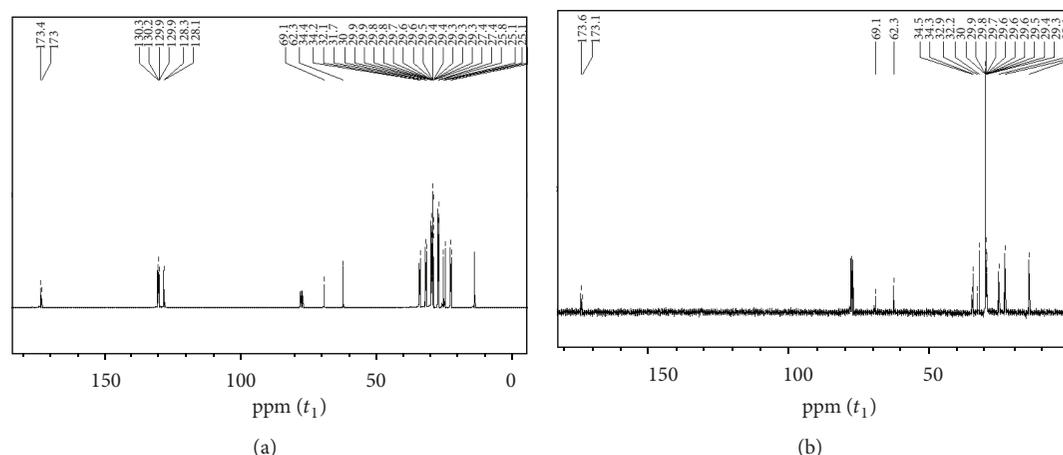


FIGURE 2: Comparison of the 75 MHz ^{13}C -NMR spectra of sunflower oil (a) and hydrogenated sunflower oil (b) in CDCl_3 solutions.

After the sunflower oil was hydrogenated with SAC successfully, the hazelnut oil and tea seed oil were hydrogenated with the same procedures and similar results were observed. The iodine values were given in Table 1.

4. Conclusions

In conclusion, we have developed a process-friendly, efficient, cheap, and green procedure for the hydrogenation of sunflower oil catalyzed by scrap automobile catalyst (SAC) and this hydrogenation procedure was performed on the hazelnut oil and tea seed oil successfully. This method can be used in the fats, oils, and chemical industry.

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