Continuous Ultrasonic Hydrogenation of Soybean Oil. II. Operating Conditions and Oil Quality

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In previous work we found that ultrasonic energy greatly enhanced the rate of hydrogenation of soybean oil. We have now investigated parameters of ultrasonic hydrogenation and the quality of the resulting products. Refined and bleached soybean oil was hydrogenated continuously with and without ultrasonic energy at different temperatures, pressures and catalyst concentrations. Flavor and oxidative stability of the oils were compared with a commercially hydrogenated soybean oil. The extent of hydrogenation (ΔIV) was not affected by temperature between 245 and 290 C, but was greater at 106 psig than at 65 psig hydrogen pressure. The ΔIV of hydrogenated oils increased linearly with catalyst concentration from 40 ppm to 150 ppm nickel. At the same catalyst concentration the IV drop was significantly increased when ultrasonic energy was used. By reducing the amount of power supplied to the ultrasonic reactor to 40% of full power, the specific power (watts/ΔIV) was lowered by 60%. Linolenate selectivities and specific isomerization (% *trans*/ΔIV) remained the same, but linoleate selectivities were lower than for batch hydrogenation under varied operating parameters. Flavor scores were not significantly different, initially or after storage eight days at 60 C, for oils continuously hydrogenated with and without ultrasonic energy. Hydrogenation of soybean oil with ultrasonic energy offers a method to produce good quality products at potentially lower cost than present methods.

In a previous report (1) we noted that the rate of continuous hydrogenation of soybean oil with copper or nickel catalyst slurry greatly increased with application of ultrasonic energy. It was difficult to determine whether the effect of ultrasonic energy was due to elevated temperature or improved oil/catalyst/hydrogen contact in the reaction zone. In the present study the extent of hydrogenation (ΔIV) at elevated temperature with ultrasonic energy was compared with that observed without ultrasonic energy. Oils hydrogenated continuously with and without ultrasonic energy were evaluated by a taste panel and compared with a commercially hydrogenated soybean oil.

EXPERIMENTAL

Figure 1 presents a flow sheet for the continuous hydrogenation of soybean oil. Commercially refined and bleached soybean oil (Anderson Clayton Foods, Richardson, Texas) and Nysel® catalyst (25% nickel in stearin) (Harshaw/Filtrol Partnership, Cleveland, Ohio) were mixed (A) and filtered through a 10-μ filter (to prevent damage to the flow transducer), pumped (B) at 1 l/hr through heat exchangers (C), an ultrasonic processing cell (2.4 ml effective reaction zone) (D) (Branson Sonic Power Co., Danbury, Connecticut) to receiver (E) (Jerguson Gauge and Valve Co., Burlington, Massachusetts). An ultrasonic converter changes electrical energy to mechanical vibrations, and a booster horn modifies the mechanical amplitude in the processing cell. The hydrogenated product was separated from the excess hydrogen in the receiver and withdrawn continuously (J). Oil and catalyst in charger (A) were constantly mixed by stirrer and nitrogen bubbling. However, part of the catalyst settled out, and the concentration of catalyst in oil reaching the processing cell (D) was less than originally formulated. Concentration of nickel in the slurry actually hydrogenated was, therefore, determined by analyzing this slurry for nickel after hydrogenation. Hydrogen pressure in the system was controlled by a back-pressure regulating valve (I) in the vent line. An amplitude-decreasing booster horn (ratio 1:0.4), between the ultrasonic converter and the one-in. titanium processing horn, was required to prevent overloading the power supply and thereby insure constant and effective ultrasonic action in the processing cell. Cool air was circulated in the ultrasonic converter jacket to protect the converter from heat from the processing cell. Temperatures of the oil/catalyst slurry were measured with thermocouples in the inlet line (TC I), under the processing horn (TC R) and in the outlet line (TC O). If required, additional heat was applied to the processing cell by heating tape (F). Hydrogen was introduced coaxially into the slurry directly beneath the processing horn (G). Ultrasonic power was supplied from a 550-watt, 20-kHz power supply (K) (Branson Sonic Power Co., Danbury, Connecticut). When a product with low IV was required for continuous hydrogenation, the oil-catalyst slurry was collected and recycled as needed to reach the desired IV.

Adjustment of the power control varied the power supply voltage and the amplitude of mechanical vibration to the slurry in the processing cell. A loading meter indicated the level of ultrasonic power transmitted to the processing horn. Power (watts) required to hydrogenate soybean oil was calculated by the product of the output power to the converter (550 watts X power control setting, %) and the loading meter reading (%). The ultrasonic energy used during continuous hydrogenation at steady state to drop the IV one unit was calculated as specific power by dividing the power by the ΔIV (watt/ΔIV).

To study the effects of temperature and of ultrasonic energy independently during hydrogenation, the same lot of refined and bleached soybean oil was hydrogenated in a batch with a two-l stirred autoclave (Parr Instrument Co., Moline, Illinois) at the same conditions as in the continuous hydrogenation equipment.

For flavor evaluation, experimental and commercial

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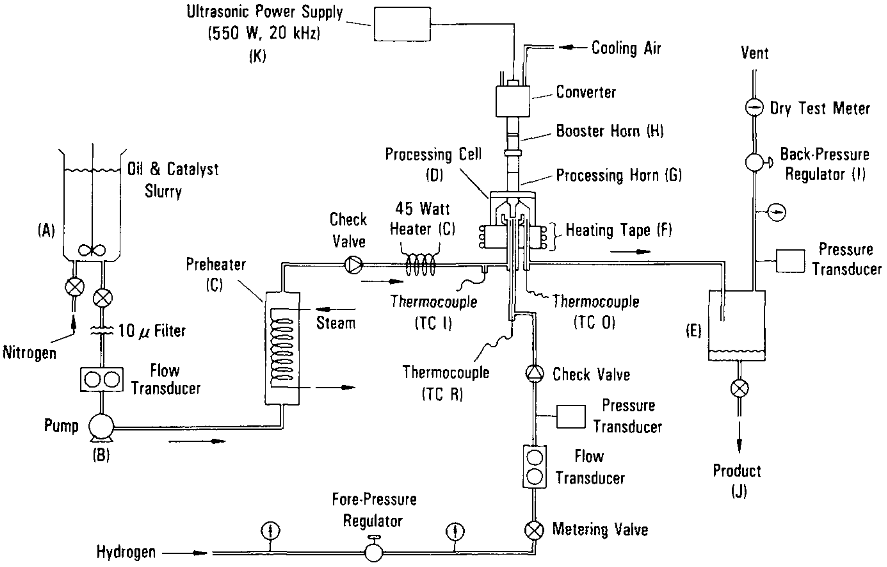

FIG. 1. Schematic flowsheet for the continuous ultrasonic hydrogenation of soybean oil.

hydrogenated oils were post-bleached and then deodorized simultaneously in a four-place glass deodorizer (2) at 220 C, 0.5 mm vacuum, 5% sparge steam for three hr. Deodorized oils were treated with 100 ppm citric acid (CA) during the cooling period. Oils were evaluated by an experienced 15-member taste panel using a flavor scale from 1 to 10 (where 1 = extreme poor flavor; 10 = bland flavor). Scores were computed statistically by analysis of variance (3).

Methyl esters of oil samples were analyzed for fatty acid composition by gas chromatography with a packed column (4). *Trans* isomers, conjugated diene and peroxide value (PV) were analyzed by AOCS Official Methods (5). Measurement of nickel in the slurry after hydrogenation was determined by Atomic Absorption Spectroscopy (6).

RESULTS

A series of 18 single-pass hydrogenations was conducted to determine the effect of temperature (270 and 290 C), pressure (65 and 106 psig), catalyst concentration (40, 80, 120, 150 ppm Ni), and ultrasonic power level (100, 40 and 0% of full power). For all hydrogenations the pump rate was set so the residence time in the reactor was 9 seconds/pass.

Figure 2 illustrates the actual recorder temperature

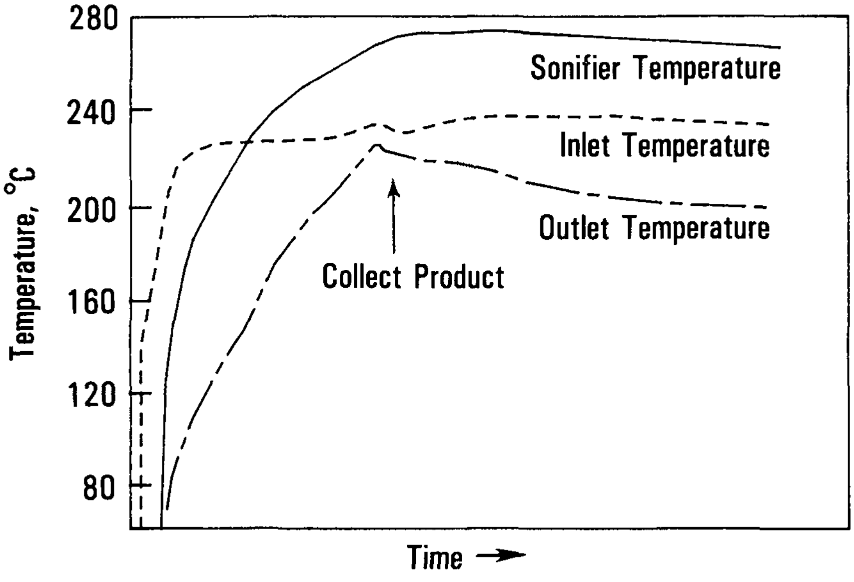

FIG. 2. Typical temperature profile of continuous ultrasonic hydrogenation.

TABLE 1

Continuous Hydrogenation of Soybean Oil

	Run no. (Ultrasonic hydrogenation)									
	1	2	3	4	5	6	7	8	9	10
Hydrogenation conditions										
Temperature, C	270	270	270	270	290	290	290	290	270	270
Pressure, psig	65	65	65	65	65	65	65	65	106	106
Catalyst, ppm Ni	150	120	80	40	150	120	80	40	120	80
Reaction time, sec.	9	9	9	9	9	9	9	9	9	9
Power control setting, %	100	100	100	100	100	100	100	100	100	100
Hydrogenation rate, ΔIV/sec	4.3	3.4	2.6	1.0	4.2	3.8	2.2	1.3	4.0	3.3
Analysis										
Fatty acid composition, %[a]										
Saturates	17.3	16.3	15.8	15.3	18.0	17.1	16.5	15.5	18.0	17.2
Monoene	56.7	49.8	43.1	30.6	53.5	51.3	38.9	32.4	52.3	47.4
Diene	24.0	30.9	37.1	47.6	26.0	28.9	39.7	46.2	27.1	32.0
Triene	2.0	3.0	4.0	6.5	2.4	2.7	4.8	5.9	2.6	3.4
trans, %	24	21	18	9	27	20	12	8	22	19
IV	96	104	112	126	97	101	115	123	99	105
ΔIV	39	31	23	9	38	34	20	12	36	30
Specific isomerization, % *trans*/ ΔIV	0.6	0.7	0.8	1.0	0.7	0.6	0.6	0.7	0.6	0.6
Selectivity ratio										
K_{Ln}/K_{Lo}[b]	1.5	1.4	1.5	1.4	1.4	1.5	1.4	1.6	1.4	1.4
K_{Lo}/K_{01}[c]	16	23	20	15	15	15	13	14	12	11

	Run no. (Ultrasonic hydrogenation)							Run no. (Non-ultrasonic hydrogenation)	
	11	12	13	14	15	16	17	18	19
Hydrogenation conditions									
Temperature, C	270	290	290	290	290	245	276	245	182
Pressure, psig	106	106	106	106	106	106	106	106	106
Catalyst, ppm Ni	40	150	120	80	40	80	150	80	60
Reaction time, sec.	9	9	9	9	9	9	9	9	480
Power control setting, %	100	100	100	100	100	100	40	0	0
Hydrogenation rate, ΔIV/sec	1.7	4.9	4.6	3.0	1.8	2.9	5.1	2.0	0.1
Analysis									
Fatty acid composition, %[a]									
Saturates	16.2	20.4	18.1	17.5	16.0	16.7	19.1	16.6	19.6
Monoene	34.8	56.3	56.1	43.8	35.5	44.5	58.4	36.7	56.2
Diene	43.4	21.2	23.0	34.6	43.0	35.1	19.9	41.6	22.6
Triene	5.6	2.1	2.1	4.1	5.9	3.7	1.8	5.1	1.6
trans, %	12	27	23	16	9	16	27	11	20
IV	120	91	94	108	119	109	89	117	92
ΔIV	15	44	41	27	16	26	46	18	43
Specific isomerization, % *trans*/ ΔIV	0.8	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.5
Selectivity ratio									
K_{Ln}/K_{Lo}[b]	1.4	1.2	1.3	1.3	1.6	1.5	1.3	1.4	1.6
K_{Lo}/K_{01}[c]	10	11	11	9	9	11	10	7	8

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[a] Starting soybean oil: saturates, 14.0%; monoene, 22.6%; diene, 54.2%; triene, 8.2%; IV, 135.

[b] Linolenate selectivity.

[c] Linoleate selectivity.

profile obtained during the continuous ultrasonic hydrogenation of soybean oil. In this example the inlet oil was preheated to 230 C and the temperature remained constant throughout the run. As soon as power to the processing horn was started the incoming slurry temperature (TC I) increased rapidly to 270 C in the processing cell (TC R) and remained constant thereafter. The hydrogenation temperature in the processing cell was regulated by varying the temperature of the inlet slurry (TC I). The oil product was collected continuously when steady state was reached. The outlet temperature (TC O) was much lower than the reaction temperature (TC R) or inlet temperature (TC I). Although the processing cell was well insulated, some heat may have been dissipated through the walls and transferred to the processing horn and booster horn.

Regression lines for reactions at 270 C and 290 C were statistically parallel and with intercepts not significantly different from each other. Therefore, the extent of hydrogenation (ΔIV) was not affected by temperature between 270 C and 290 C (Table 1, Runs 1 to 15). On the other hand, the extent of hydrogenation was significantly affected by hydrogen pressure (Fig. 3, Table 1). The regression equation at 65 psig was $\Delta IV = 0.61 + (0.26 \times \text{catalyst concentration})$ and at 106 psig was $\Delta IV = 5.9 + (0.27 \times \text{catalyst concentration})$. Within the catalyst range used in our experiments (40-150 ppm Ni) ΔIV increased linearly with catalyst concentration. Satisfactory hydrogenation would be expected with less than 40 ppm Ni, but longer reaction time would, of course, be required.

Previous work with continuous ultrasonic hydrogenation of soybean oil showed that there were practical limits to the input power to the processing cell (1). A pressure greater than 200 psig "stalled" the ultrasonic vibrations. By connecting the converter to the processing horn (G) with a 1:1 (input to output) booster horn (H), intermittent "stalling" also resulted. By changing to a 1:0.4 booster horn, the "stalling" was nearly eliminated under our experimental conditions. When the power control was adjusted to 40% of full power the ultrasonic action was also steadied. This lowering of the power resulted in more efficient use of ultrasonic energy. Although hydrogenation rates (ΔIV/min) were similar, the energy required to drop the IV (watts/ΔIV) was much less at 40% power than at full power. Figure 4 shows that the specific power was 7 watts/ΔIV when oil was hydrogenated with 80 ppm Ni and full power; 2.5 watts/ΔIV with the same catalyst concentration and 40% of full power. Although these power settings may not be optimal, the results indicate that full power is not necessarily the most efficient way to hydrogenate soybean oil with ultrasonic energy.

To determine how much ultrasonic action contributed to the extent of hydrogention (ΔIV), two different methods were used. In one method, the ΔIV was compared with and without ultrasonic energy (Runs 16 and 18, Table 1). With 80 ppm Ni at 245 C and 106 psig hydrogen pressure, the ΔIV was 26 in 9 seconds with ultrasonic energy compared to ΔIV of 18, without ultrasonic energy. The rate of hydrogenation with ultrasonic energy was 1.5 times the rate without ultrasonic energy.

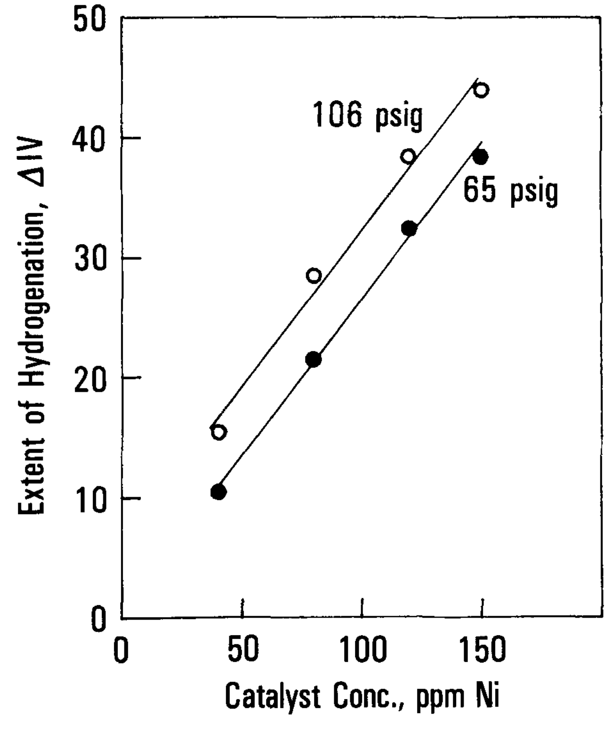

FIG. 3. Effect of nickel catalyst concentration on extent of hydrogenation (ΔIV) at two hydrogen pressures. (Temperature, 270-290 C; pressures, 65 and 106 psig; catalyst, 50-150 ppm Ni.)

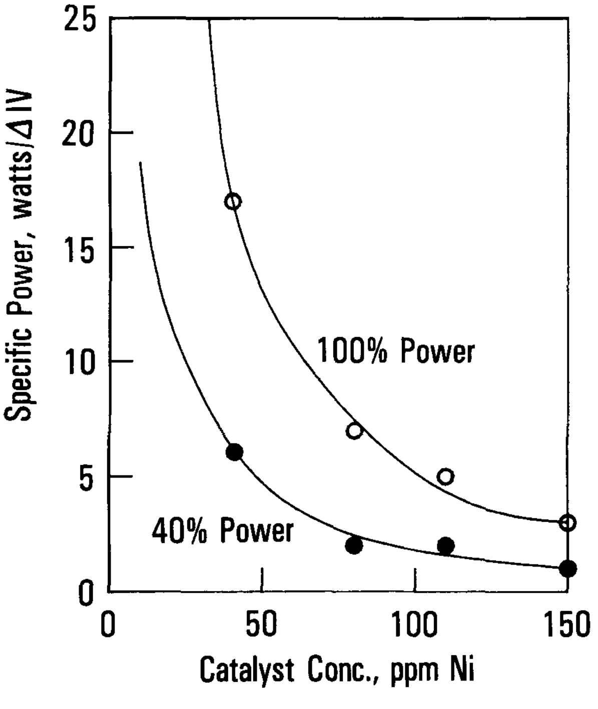

FIG. 4. Effect of varying the power applied to the processing horn on the specific power (watts/ΔIV) at varied catalyst concentrations. (Hydrogenation temperature, 270 C; pressure, 65 psig; catalyst, 50-150 ppm Ni.)

TABLE 2

Continuous Ultrasonic Hydrogenation vs Batch Hydrogenation of Soybean Oil[a]

	Continuous ultrasonic hydrogenation			Batch hydrogenation		
Run no.	20	20	20	21	21	21
Conditions						
Time, sec.	9	18	27	180	300	480
Hydrogenation rate, ΔIV/sec	2.0	1.8	1.1	0.10	0.13	0.12
Analysis						
Fatty acid composition, %[b]						
Saturates	15.3	17.4	19.5	15.1	15.6	19.6
Monoene	39.4	51.1	56.9	40.6	54.2	67.8
Diene	40.4	28.7	21.8	40.1	28.1	12.6
Triene	4.9	2.8	1.8	4.2	2.1	0
trans isomers, %	12	21	25	15	20	28
IV	117	101	91	116	101	80
ΔIV	18	34	44	19	34	55
Selectivity ratio						
K_{Ln}/K_{Lo}	1.4	1.4	1.4	1.7	1.7	—
K_{Lo}/K_{01}	12	10	9	26	34	18

[a] Conditions for both hydrogenations: Catalyst, 80 ppm Ni; temperature, 233 C; pressure, 112 psig.

[b] Starting oil, see Table 1, footnote a.

In the second method, soybean oil was hydrogenated in a stirred batch autoclave and the results were compared with those of continuous ultrasonic hydrogenation (runs 20 and 21, Table 2 and Fig. 5). With 80 ppm Ni at 233 C and 112 psig hydrogen pressure, the hydrogenation rate, ΔIV/sec was 2.0 with ultrasonic energy compared with a ΔIV/sec of 0.10 by batch hydrogenation without ultrasonic energy. The rate of ultrasonic hydrogenation was 20 times higher than batch hydrogenation without ultrasonic energy.

Linolenate selectivity (K_{Ln}/K_{Lo}) ranged from 1.2 to 1.7 from continuous ultrasonic hydrogenation, continuous non-ultrasonic hydrogenation and batch non-ultrasonic hydrogenation. Linoleate selectivity (K_{Lo}/K_{01}), however, was lower for continuous ultrasonic and continuous non-ultrasonic hydrogenation than for batch non-ultrasonic hydrogenation at the same IV. The specific isomerization (% *trans*/ΔIV) obtained with both methods was relatively constant.

Table 3 compares flavor scores and peroxide values of oils hydrogenated continuously with ultrasonic energy (Run 17), without ultrasonic energy (Run 19), and a commercially hydrogenated oil. These test oils and the commercial oil were chosen for flavor evaluation because of their similar composition. The linolenate content for all three oils ranged from 1.6 to 2.0%. Oil from Run 18, which was hydrogenated without ultrasonic energy, was not used as a control because it contained 5.1% linolenate. Initially (0-time), all oils were rated as good quality, with flavor scores from 7.0 to 7.7, and were not significantly different. Flavor descriptions given by the panel were mainly nutty and

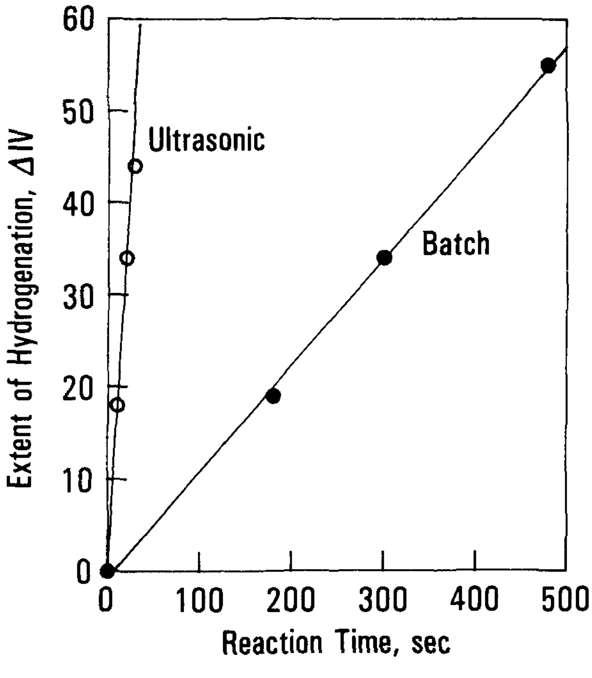

FIG. 5. Comparison of rates of continuous hydrogenation with batch hydrogenation of soybean oil. (Hydrogenation temperature, 233 C; pressure 112 psig; catalyst, 80 ppm Ni.)

TABLE 3

Flavor Evaluation of Hydrogenated Soybean Oils (HSBO)

	Flavor scores				
	Continuous ultrasonic HSBO		Continuous non-ultrasonic HSBO		Commercial HSBO[a]
Run no.	17[b]		19[b]		
Storage conditions					
0-time	7.4(0.1)[c]	n.s.	7.6(0.1)		—
	7.0(0.1)		n.s.		7.7(0.1)
8 days at 60 C	6.6(1.8)	n.s.	7.0(2.7)	*	5.8(3.0)
	6.6(1.8)		*		5.6(2.9)

[a] Fatty acid composition: Saturates, 15.8%; monoene, 53.6%; diene, 28.6%; triene, 2.0%; IV, 101.

[b] See Table 1 for hydrogenation conditions and analysis.

[c] Peroxide value, me/Kg (in parentheses).

n.s., No significant difference between flavor scores.

*, Significantly different flavor scores at 95% confidence level.

buttery initially for these oils. Peroxide values were 0.1 me/Kg for all oils. After storage for eight days at 60 C, flavor scores from the oils of Runs 17 and 19 were slightly lower than initial scores, indicating good flavor stability. No significant difference was noted between oils of Run 17 and 19. Flavor descriptions for these stored oils included nutty and buttery for Run 17 oil; nutty, buttery, rancid and beany for Run 19 oil; and buttery, beany, metallic and rancid for the commercially hydrogenated oil. Flavor stability of the stored commercial hydrogenated oil was significantly less than the oils of Run 17 and 19. Peroxide value of stored Run 17 oil was lower than that of Run 19 and the commercially hydrogenated oil.

This study showed that soybean oil can be continuously and rapidly hydrogenated with ultrasonic energy using a small amount of nickel catalyst. In previous work (1), we assumed the outlet temperature to be the same as the reaction temperature, and ultrasonic and non-ultrasonic hydrogenations were compared at this temperature. However, as shown in Figure 2, the outlet temperature was considerably lower than the reaction temperature. Therefore, the increased rate of hydrogenation previously reported (ca. 100 ×) was not only the result of ultrasonic energy but partly due to a much higher temperature developed in the processing cell. The present study shows that ultrasonic power does increase the rate of hydrogenation (20 ×) when compared with batch runs carried out at the same temperature.

Many reasons have been suggested (7,8) for the effect of ultrasonic energy in increasing reaction rates. Chemical processes are known to be accelerated at energy above the threshold ultrasonic intensity. At this intensity level shock waves within the liquid cause cavitation, which subjects liquids to rapidly alternating pressures. The resulting very high localized pressures beneath the ultrasonic horn are accompanied by very high temperatures. Small gas bubbles and fine particulate matter may form nuclei to assist cavitation. Furthermore, rapid continuous oil flow into and out of the reaction zone may minimize back-mixing, prevalent in many continuous processes. Soybean oil, continuously hydrogenated in this study with ultrasonic energy, was shown to be of good flavor quality.

ACKNOWLEDGMENTS

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