Continuous Slurry Hydrogenation of Soybean Oil with Copper-Chromite Catalyst at High Pressure[1]

S. KORITALA, K.J. MOULTON, SR., J.P. FRIEDRICH, E.N. FRANKEL and
W.F. KWOLEK[2], Northern Regional Research Center, Agricultural Research Service,
USDA, Peoria, IL 61604

ABSTRACT

Selective hydrogenation of soybean oil to reduce linolenic acid is accomplished better with copper than with nickel catalysts. However, the low activity of copper catalysts at low pressure and the high cost of batch equipment for high-pressure hydrogenation has precluded their commercial use so far. To evaluate continuous systems as an alternative, soybean oil was hydrogenated in a 120 ft × 1/8 in. tubular reactor with copper catalyst. A series of hydrogenations were performed according to a statistical design by varying processing conditions: oil flow (0.5 L/hr, 1.0 L/hr and 2.0 L/hr), reaction temperature (180 C and 200 C), hydrogen pressure (1,100 psig and 4,500 psig) and catalyst concentration (0.5% and 1.0%). An iodine value (IV) drop of 8-43 units was observed in the products whereas selectivity varied between 7 and 9. Isomerization was comparable to that observed with a batch reactor. Analysis of variance for isomerization indicated interaction between catalyst concentration and hydrogen pressure and between catalyst concentration and temperature. The influence of pressure on linolenate selectivity was different for different temperatures and pressure. Hydrogenation rate was significantly affected by pressure, temperature and catalyst concentration.

INTRODUCTION

Hydrogenation of soybean oil improves its resistance to oxidative and flavor deterioration (1). Copper catalysts are much more selective than commercially employed nickel catalyst for the reduction of linolenic acid (2). However, the lower activity of copper catalysts makes their use uneconomical. Furthermore, copper catalysts produce undesirable conjugated dienes that are eliminated at high pressures (3). The activity of copper catalysts in batch reactors was previously shown to increase at higher pressures without loss of selectivity (3). However, the cost of batch equipment for hydrogenation at high pressures becomes prohibitive. The cost disadvantage could probably be minimized with a continuous system employing a tubular reactor with high throughput. The feasibility of such a reactor operating at low pressures (500 psi) has been demonstrated (4). A new reactor was designed to operate at pressures higher than 500 psig to check the feasibility of continuous hydrogenation at high pressures and to determine their effect on the selectivity and reactivity of copper catalysts. This paper reports on a continuous slurry reactor operable at pressures up to 5,000 psig. The effect of operation variables, e.g., oil flow rate, temperature of reaction, hydrogen pressure and catalyst concentration, on the characteristics of the hydrogenated products was studied.

EXPERIMENTAL PROCEDURES

Apparatus

The slurry system, consisting of the charger, reactor, sampler and receiver, is shown in Figure 1. The oil-catalyst

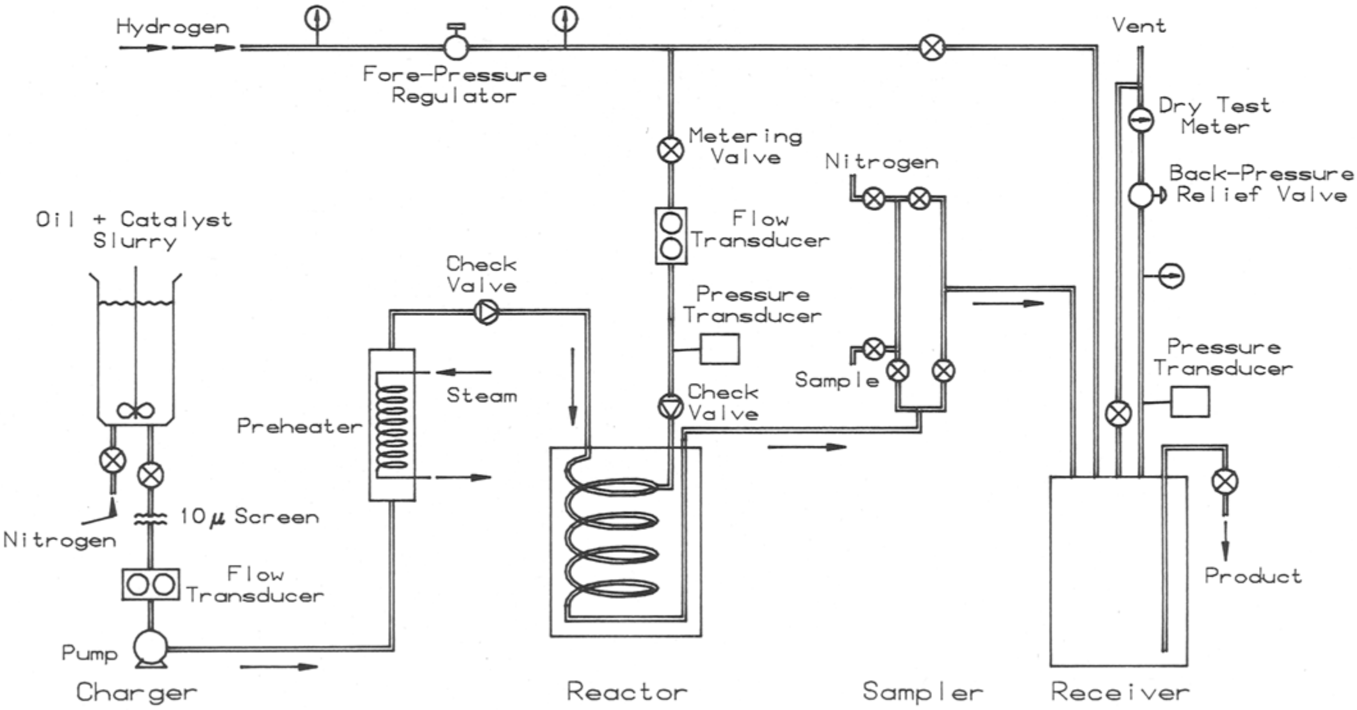

FIG. 1. Schematic diagram for continuous slurry hydrogenation.

---

[1] Presented at AOCS meeting, Chicago, May 1983.

[2] Biometrician, North Central Region, Agricultural Research Service, USDA stationed at the NRRC.

mixture was stirred while nitrogen was bubbled through it. The slurry was pumped into the reactor through a preheater. A flow transducer enabled continuous recording of the flow rate, which could be varied by adjusting the pump stroke. The reactor consisted of a 1/8 in. × 120 ft coiled stainless-steel tube (0.085 in. i.d.). At intervals of 5 ft, 10 ft, 20 ft, 30 ft, 45 ft, 60 ft, 75 ft, 95 ft and 120 ft from the point of introduction of hydrogen, 4-port high-pressure fittings were installed to allow diversion of the slurry at the desired length of the reactor. Thermocuples were installed at each of the 9 ports to monitor the temperature. Ca. 5 ft from the point of entry of the oil-catalyst slurry into the reactor, hydrogen gas was introduced concurrently with the slurry flow through a syringe needle. A metering valve allowed control of gas flow, which was continuously monitored through a flow transducer. The reactor was installed inside a 3-gal high-pressure vessel and heated with high-pressure steam. The oil-catalyst-gas mixture flowed into a 1-gal receiver through a sampler loop. A 2-mL sample could be trapped in the sampler loop and removed without upsetting the equilibrium by mainpulating a series of valves. A back-pressure relief valve provided the proper regulation of pressure in the receiver and the reactor.

Materials

A single lot of commercially refined and bleached soybean oil, which was stored at 34 F, was used in all the experiments. The fatty acid composition was: 16:0, 11.0%; 18:0, 3.6%; 18:1, 23.0%; 18:2, 54.9%; 18:3, 7.5%. Calculated iodine value (IV) of the oil was 134.5. Copper-chromite catalyst (Cu1106-P, 39% CuO, 43.5% Cr_2O_3, 10% BaO) was furnished by Harshaw Chemical Co., Beachwood, OH.

Methods

For each hydrogenation, 5-9 samples were obtained from different ports in the reactor. Methyl esters of fatty acids were prepared by sodium methoxide-catalyzed transesterification of triglycerides with methanol (5). Fatty acid composition was determined by gas liquid chromatography (GLC) with packed columns (EGSS-X) and the IV was calculated. The percentage of isolated *trans* was measured by comparing the infrared absorption of methyl esters at 966 cm^{-1} with methyl elaidate standard. Linolenate-to-linoleate selectivity ratios (K_{Le}/K_{Lo}) were determined by a digital computer assuming consecutive reactions, i.e., triene→diene→monoene (6). The average selectivity ratio and isomerization (% *trans*/ΔIV) were calculated for each hydrogenation.

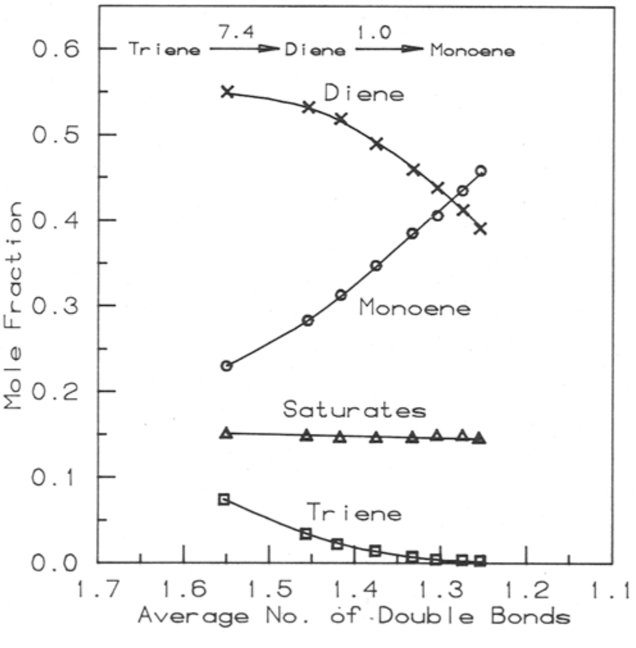

FIG. 2. Change in fatty acid composition during continuous slurry hydrogenation of soybean oil at 4,500 psi, 200 C, 0.5% copper chromite and 1 L/hr oil flow.

Residence Time

The exact time the oil and catalyst remained in the reactor could not be determined, because the volume occupied by hydrogen varies with temperature, pressure and the extent of reaction. However, the approximate residence time (RT) was calculated according to the following equation:

$$RT = V_R/(V_g + V_o)$$

where RT = residence time in minutes; V_g and V_o are the flow rates in mL/min for gas and oil and V_R is the volume of the reactor. The volume of the gas in the reactor was calculated from the flow rate, assuming that the ideal gas laws were obeyed. Hydrogen consumed during the reaction increased the residence time for the oil. On the other hand, the increase in volume of gas caused by the pressure drop across the reactor (ca 100 psig) decreased the residence time for the oil. Thus, these 2 factors tended to cancel each other. The amount of gas dissolved in the oil was assumed to be too small to affect the residence time of the oil.

RESULTS

The effect of different operating variables on the course of hydrogenation and the characteristics of the products formed was studied. Twenty-four statistically designed hydrogenations were performed (nonrandom) at 2 temperatures (180 C and 200 C), 2 pressures (1,100 psig and 4,500 psig), 2 catalyst concentrations (0.5% and 1.0%) and 3 oil flow rates (0.5 L/hr, 1.0 L/hr and 2.0 L/hr). Changing the gas flow rate between 1-4 L/min had a minimal effect on the IV of the final sample and therefore was kept constant at 1 L/min. Figure 2 shows the change in fatty acid composition for one such typical hydrogenation at 200 C, 4,500 psig with 0.5% catalyst and an oil flow rate of 1 L/hr. Although the change in fatty acid composition was plotted against the average number of double bonds (IV), each fatty acid composition represented a sample from a different length of the reactor, with the final sample having resided in the entire length of the reactor. Fatty acid compositions of decreasing unsaturation resulted as the reactor length (residence time) was increased. The final sample (IV = 108) contained 0.4% linolenic acid after a reaction (residence) time of 6.2 min. The overall reaction had an average linolenate selectivity of 7.4 and produced no increase in stearate.

A typical rate curve for hydrogenation at 1,100 psig is shown in Figure 3, where ΔIV was plotted against residence time. The rate continuously decreased with an increase in residence time. The slope of the tangent drawn to the linear portion of the curve represented the initial reaction rate for that hydrogenation.

The selectivity ratio (K_{Le}/K_{Lo}), isomerization (percentage of *trans*/ΔIV) and reaction rate (ΔIV/min) for all 24 experiments are given in Figures 4-6. The selectivity of reaction was not influenced by temperature, but higher catalyst concentration improved the selectivity of the reaction at the lower pressure. At 1,100 psig, a selectivity

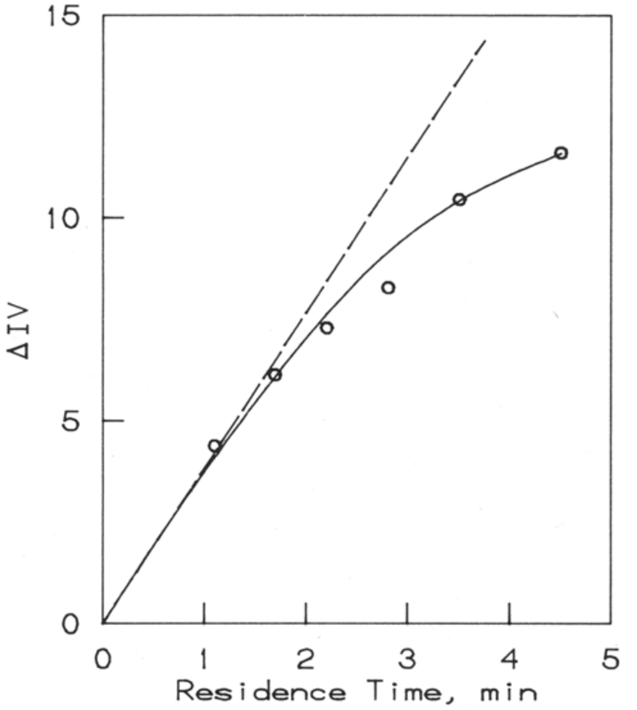

FIG. 3. Continuous slurry hydrogenation of soybean oil at 200 C, 1,100 psig, 0.5% copper chromite and 0.5 L/hr oil flow: effect of residence time on change in iodine value.

ratio of 8-9 was achieved, whereas at the higher pressure, this value decreased to 7-8. At these high selectivity ratios, very little change in fatty acid composition was observed when the selectivity ratio changed by 1 unit. Thus, from a practical standpoint, these selectivity ratios gave almost the same fatty acid composition.

Isomerization was least influenced by the different variables. Higher temperatures or lower pressures generally favor the formation of isomers (1). However, no such trend was observed. As the temperature increased from 180 C to 200 C at 1,100 psig, isomerization remained the same in one instance (1% catalyst concentration, 0.5 L/hr oil flow) and decreased in 2 cases (1% catalyst; 1 L/hr and 2 L/hr oil flow). In all other experiments at 1,100 psig, isomerization increased slightly, but the increase was too small to be of practical significance. For example, a decrease in isomerization of 0.04 represents 0.8% *trans* in a hydrogenated sample with a 20 IV drop. Higher catalyst concentration increased isomerization in most cases. At 4,500 psig, where the extent of hydrogenation was greatest, very nearly the same isomerization values are obtained regardless of temperature, catalyst concentration or oil flow rate.

The greatest change was noticeable in the rate of reaction. The rate doubled when temperature was increased from 180 C to 200 C. In most cases, raising the pressure from 1,100 psig to 4,500 psig increased the reaction rate, but not as much as that caused by the increase in temperature. In a few cases, the rate more than doubled. No significant change in the rate occurred when oil flow increased from 0.5 L/hr to 2 L/hr.

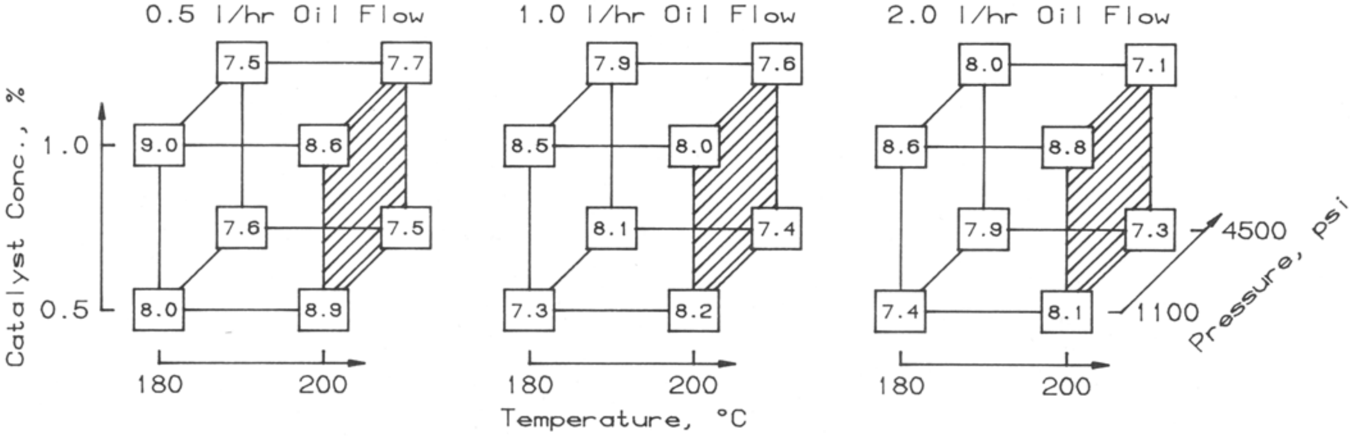

FIG. 4. Effect of change in conditions on linolenate selectivity (K_{Le}/K_{Lo}) during continuous slurry hydrogenation of soybean oil (standard deviation = 0.4).

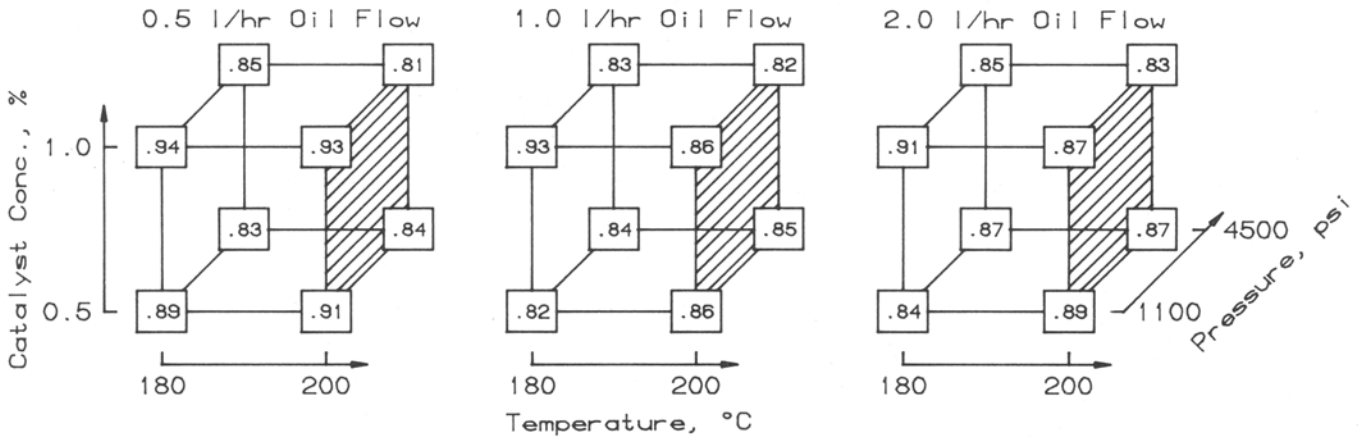

FIG. 5. Effect of change in conditions on isomerization (% *trans*/ΔIV) during continuous slurry hydrogenation of soybean oil (standard deviation = 0.02).

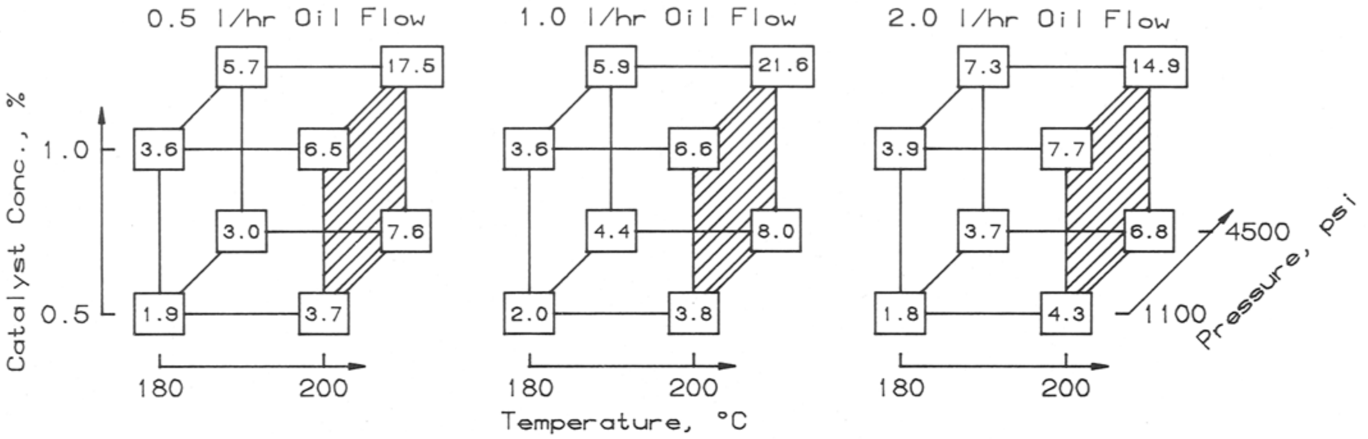

FIG. 6. Effect of change in conditions on rate of hydrogenation (ΔIV/min) during continuous slurry hydrogenation of soybean oil (relative standard deviation = 16%).

TABLE I

Significant[a] Interactions in the Analysis of Selectivity (K_{Le}/K_{Lo}) Ratio

	Temperature, C	
H_2 pressure, psig	180	200
1,100	8.1	8.4
4,500	7.8	7.4
	Catalyst concentration,%	
	0.5	1.0
1,100	8.0	8.6
4,500	7.6	7.6

Standard error of a mean = 0.14.
Least significant difference (0.05 level) = 0.5

[a] Temperature and pressure at 0.05 level, catalyst and pressure at 0.10 level.

TABLE II

Significant[a] Interaction in the Analysis of Isomerization (% *trans*/ΔIV)

	Catalyst concentration, %	
H_2 pressure, psig	0.5	1.0
1,100	0.87	0.91
4,500	0.85	0.84

Standard error of a mean = 0.007.
LSD (0.05 level) = 0.02

	Catalyst concentration, %	
Temperature, C	0.5	1.0
180	0.85	0.89
200	0.87	0.85

Standard error of a mean = 0.007.
LSD (0.05 level) = 0.02.

	H_2 pressure, psig	
Oil flow, L/hr	1,100	4,500
0.5	0.92	0.83
1.0	0.87	0.84
2.0	0.88	0.86

Standard error of mean = 0.008.
LSD (0.05 level) = 0.03.

[a] Significant at 0.01 level.

TABLE III

Mean Reaction Rate (ΔIV/min) for Four Factors

Factor	Level	Mean[a] reaction rate
Temperature, C	180	3.56
	200	7.74
Pressure, psig	1,100	3.71
	4,500	7.41
Catalyst concentration, %	0.5	3.78
	1.0	7.29
Oil flow, L/hr	0.5	4.98
	1.0	5.46
	2.0	5.31

[a] Least significant ratio (0.05 level) is 1.15 for 2-level factors.

Data in Figures 4-6 were also examined by the analysis of variance (Tables I-III). Four variables (temperature, catalyst concentration, pressure and oil flow rate) were used, and the analyses estimated variation associated with each factor and all 6, 2-way interactions. Three- and 4-way interactions were combined to obtain a variance for testing significance.

Analysis of selectivity ratio (Table I) produced 2 significant interactions, between pressure and temperature and between pressure and catalyst concentration. The effect of pressure on selectivity was greater at the higher temperature or catalyst concentration. Analysis of isomerization (Table II) showed interaction between pressure and catalyst concentration and between temperature and catalyst concentration. The decrease in isomerization with the increase in pressure was significantly greater at the higher catalyst concentration. Catalyst concentration influenced isomerization significantly at 180 C but not at 200 C. Interaction between oil flow rate and pressure suggested that isomerization was significantly affected by pressure at 0.5 L/hr oil flow.

Hydrogenation rates (Table III) were significantly affected by pressure, temperature and catalyst concentration, whereas oil flow rate had no influence. Unlike selectivity and isomerization, hydrogenation rate showed no 3- and 4-way interactions. From that data, the following equation, which describes the relationship between hydrogenation rate and the factors affecting it, was developed:

$$\text{Rate } (\Delta IV/\text{min}) = 0.0006953\ (1.0396)^{T}\ (1.0205)^{P/100}\ (3.7202)^{C}$$

where T = temperature, C; P = Pressure, psig and C = catalyst concentration, %. This equation gave a calculated rate of 1.8 IV units/min for hydrogenation at 180 C, 1,100 psig and 0.5% catalyst concentration, compared with 1.9, 2.0 and 1.8 obtained experimentally (Fig. 6).

DISCUSSION

One object of our study was to design a continuous slurry reactor capable of operating at high pressures (up to 5,000 psig and to determine the feasibility of its operation. At 180 C, 1,100 psig and 0.5 L/hr oil flow, the IV dropped 6 and 10 units for 0.5 and 1% catalyst; linolenic acid decreased to 4 and 2%. By increasing the temperature to 200 C, the IV drop increased to 12-16 units. Although this amount of IV drop is sufficient for salad oil production because the linolenate content dropped to 1%, further hydrogenation is necessary for the production of shortening and cooking oil. This was accomplished at the higher pressure. Iodine values of hydrogenated products were 17-43 units less than the original oil, depending on temperature and catalyst concentration. Therefore, any product within this range could be prepared by adjusting the parameters.

An attempt was made to compare continuous hydrogenation with previous results (3,7) of batch operation under similar conditions. Making exact comparisons is difficult because of slight differences in temperature, pressure and catalyst concentration and because of different lots of soybean oil used. The calculated residence times for the oil-catalyst slurry in the reactor were 4.5 min, 3.5 min and 2.4 min for 0.5 L/hr, 1.0 L/hr and 2.0 L/hr oil flow rates at 200 C and 1,100 psig. At 0.5 L/hr of oil flow, the decrease in IV was 11.7 units (Fig. 3), which compares favorably with batch hydrogenation. The residence times increased to 10, 6.2 and 3.5 min, respectively, for the 3 oil flow rates when pressure was increased to 4,500 psig. An IV drop of 23.5 units occurred at the higher pressure for a residence time of 4.5 min as read from the rate curve. Since this study was completed, another batch of oil was found to hydrogenate faster than the one used in our study. This increased activity probably was caused by better refining of the oil, which results in better removal of catalyst poisons. Copper catalysts have previously been shown to be sensitive to poisons in the oil (8). Selectivity at 1,100 psig was lower (8 vs 9) for continuous hydrogenation. But this high selectivity is still sufficient to reduce linolenic acid to less than 1% at 20 IV drop. No significant differences in isomerization were noted.

Our studies have shown that preparing salad oil as well as shortening and cooking oils is possible in a continuous system by changing hydrogenation conditions. Temperature, pressure, catalyst concentration and oil flow rate had no significant practical effect on selectivity or isomerization, but the hydrogenation rate generally increased with increase in temperature, pressure and catalyst concentration. To hydrogenate large volumes of vegetable oils at high pressure to a given IV, continuous reaction with selective copper chromite catalyst may offer economic advantages over batch hydrogenation.

REFERENCES

1. Allen, R.R., in Bailey's Industrial Oil and Fat Products, edited by D. Swern, Vol. 2, 4th edition, John Wiley & Sons, New York, 1982, pp. 1-95.
2. Koritala, S., and H.J. Dutton, JAOCS 43:556 (1966).
3. Mounts, T.L., S. Koritala, J.P. Friedrich and H.J. Dutton, JAOCS 55:402 (1978).
4. Snyder, J.M., T.L. Mounts, C.R. Scholfield and H.J. Dutton, JAOCS 59:19 (1982).
5. Birner, E.D., T.L. Mounts and H.J. Dutton, JAOCS 57:209 (1980).
6. Butterfield, R.O., and H.J. Dutton, JAOCS 44:549 (1967).
7. Koritala, S., J.P. Friedrich and T.L. Mounts, JAOCS 57:1 (1980).
8. Koritala, S., JAOCS 52:240 (1975).

[Received October 22, 1983]

Detection of Cow Milk Admixture to Buffalo Milk

R.S. FARAG, Biochemistry Department, Faculty of Agriculture, Cairo University, Egypt, **M.M. HEWEDI,** Food Industries Department, Faculty of Agriculture, El-Fayoum University, Egypt, **S.H. ABO-RAYA,** Food Science and Technology Department, Faculty of Agriculture, Cairo University, Egypt and **H.H. KHALIFA,** Animal Production Department, Faculty of Agriculture, Al-Azhar University, Egypt

ABSTRACT

A method has been devised that gives the distribution of various fatty acids of pure and adulterated buffalo milk with cow milk. Gas chromatography (GC) was used for the qualitative and quantitative determination of fatty acids of authentic buffalo milk, cow milk and buffalo milk adulterated with cow milk. The milk fat was separated by fractional crystallization at -20 C into 2 fractions, i.e., semisolid and mother liquor. The concentration of fatty acids in the mother liquor changed significantly for 14:0, 16:0 and 18:1 as adulteration levels were increased. The fatty acids of the semisolid fractions change in the proportion of 16:0, 18:0 and 18:1 when cow milk is mixed with buffalo milk. By applying simple regression equations for these acids, adulteration of buffalo milk with 5% cow milk could be distinguished.

INTRODUCTION

Buffalo milk is considerably higher priced than cow milk in Egypt. For economic as well as ethical reasons, therefore, ascertaining that buffalo milk offered for sale is free from adulteration by cow milk is desirable. Hence, a test is needed to check milk adulteration. This problem has been approached by analyzing fatty acids (1,2), unsaponifiables (3) and the ratios of some members of these lipid classes. Examining milk-protein fractions (4,5) also provides a sensitive method to detect adulteration. The present study was carried out to determine whether fatty acid analysis under certain conditions could be used as a decisive test to detect and determine the extent of adulteration of buffalo milk with cow milk.

MATERIALS AND METHODS

Milk Samples

Milk samples were collected during the winter from the Experimental Station Herd, Faculty of Agriculture, Cairo University, Giza, Egypt. The herd is comprised of Egyptian buffalos and Balady cows (30 each), 4-6 years old, that were milked twice daily. The animals were mainly fed Egyptian clover and concentrate mixtures during the winter season. Daily milk yield (morning and evening milking) was