

Technical

✦ Ultrasonic Hydrogenation of Soybean Oil

K.J. MOULTON, SR., S. KORITALA and E.N. FRANKEL, Northern Regional Research Center, Agricultural Research Service, USDA, Peoria, IL 61604

ABSTRACT

The rate of hydrogenation of soybean oil with either copper chromite or nickel catalysts increased more than a hundredfold with the aid of ultrasonication. In a continuous reaction system, the selectivity with copper catalyst for linolenate reduction was somewhat lower when ultrasonic energy was applied than when not applied. With ultrasonic energy, 87% hydrogenation of linolenate in soybean oil was obtained in 9 sec at 115 psig H₂ with 1% copper chromite at 181 C and 77% linolenate hydrogenation with 0.025% nickel. Without ultrasonic energy, only 59% linolenate hydrogenation was obtained in 240 sec with copper chromite at 198 C and 500 psig H₂ and 68% linolenate hydrogenation in 480 sec with nickel at 200 C and 115 psig H₂. This innovation may offer an important advantage in increasing the activity of commercial catalysts, particularly copper chromite, for fats and oil hydrogenation.

INTRODUCTION

Interest in the application of ultrasonic energy to chemical reactions has increased during the past 20 years with the development of powerful and efficient sonic generators (1-3). Researchers found that acoustical cavitation produced extreme localized heat and pressure under the proper conditions and enhanced a chemical reaction. However, the "proper conditions" generally require reactions in an aqueous medium or, in some cases, in organic solvents (4-6). We have now found that hydrogenation of a vegetable oil can be achieved in a three-phase, non-aqueous system (liquid oil/H₂ gas/solid catalyst). Unlike batch reactions in use at the present time that require long reaction time, the hydrogenation occurs continuously and rapidly in the system described here.

EXPERIMENTAL PROCEDURES

One percent commercial copper chromite catalyst (Cu 1106P), or 0.1% Nysel catalyst (25% Ni), (Harshaw Chemical Co., Beachwood, OH), was mixed with vacuum-dried, refined and bleached soybean oil into a slurry. This slurry was pumped at 0.5 - 2.0 L/hr through a preheater, an ultrasonic continuous processing cell and a tube reactor to a 1 gallon receiver (Fig. 1). Samples (2 mL) were withdrawn periodically from the system downstream from the reactor

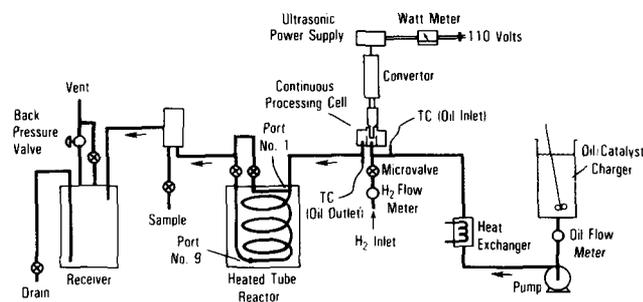


FIG. 1. Flow diagram for slurry hydrogenation of soybean oil with or without the use of ultrasonic power.

without disturbing the system equilibrium by a valve arrangement. Ultrasonic energy was supplied by a Branson Sonic Power Co. (Danbury, CT) Model J32A power supply capable of producing up to 550 W at 20 kHz. This high-frequency energy was transformed to longitudinal mechanical vibrations by the sonic convertor connecting the power supply to the probe. The probe was inserted in the processing cell in contact with the flowing slurry. The tube reactor was a 120 ft coil of 1/8 in. stainless steel tubing mounted in a 3 gallon autoclave. Nine ports, spaced nearly equidistant in the tube reactor, diverted the slurry flow and varied the reaction time. Reaction times were calculated by dividing the catalyst/oil slurry pump rate by the volume of the reaction zone, i.e., in the ultrasonic processing cell or in the tube reactor up to the discharge port. When required, the reactor was heated by steam generated within the 3 gallon autoclave. Cylinder hydrogen, 99% pure, was admitted coaxially to the catalyst/oil slurry at 1 L/min just beneath the ultrasonic probe. System pressure was maintained by regulating the back pressure valve and was measured both upstream of the processing cell and the back pressure valve. Oil samples were analyzed to determine selectivity, percentage *trans*, percentage conjugated diene and the extent of hydrogenation by packed and capillary column GC, as described previously (7).

RESULTS AND DISCUSSION

The effects of ultrasonic energy on copper chromite catalyzed hydrogenation of soybean oil are shown in Table I. In preliminary experiments, ultrasonic energy, applied at hydrogenation pressures of 200 psig and greater, did not significantly improve the catalyst activity. However, when the pressure was lowered to 115 psig, the triene in the soybean oil was selectively reduced to 1.0% within 9 sec in the ultrasonic cell reaction zone at 181 C. Apparently the ultrasonic vibrations "stalled" at 200 psig, but the lower pressure of 115psig produced more cavitation and thus more hydrogenation. Under these conditions, a lower linolenate selectivity of 5-7 was observed compared to 10 in a batch hydrogenation at similar pressure (8). At iodine value (IV) of 112, 1.6% conjugated diene was detected, which was greater than with a batch hydrogenation. As shown in Table I for nickel-catalyzed hydrogenation of soybean oil with ultrasonic energy applied at a hydrogenation pressure of 115 psig and 183 C, the triene was reduced in 9 sec to 1.7% to a product with an IV of 94. *Trans* isomer and percentage *trans* per Δ IV values are lower than those in a batch hydrogenation (8). The significant increase in rate of hydrogenation may be due to a combination of high localized temperature and pressure, improved hydrogen/oil/catalyst contact and better hydrogen dispersion. Under the conditions used in this study, back mixing in the cell may have caused the lower triene selectivities observed.

Using the same equipment without ultrasonic power and with copper chromite at 198 C and 500 psig hydrogenation pressure, only 4% of the triene in the soybean oil was hydro-

TABLE I

Hydrogenation of soybean oil

Reaction time, sec (flow rate, L/hr)	Temp of oil sonifier (C)	GC analysis (%)					Calc ^a IV	IR analysis % <i>trans</i>	Percent <i>trans</i> Δ IV	Selectivity	
		Saturate	Monoene	Diene	Conj. diene	Triene				K _{Ln} /K _{Lo}	K _{Lo} /K _{O1}
Starting soybean oil	—	14.6	23.0	54.9	—	7.5	134	—	—	—	—
Reaction <i>with</i> sonifier Copper chromite catalyst ^b											
9 ^c (1)	164	15.0	31.9	49.5	1.3	2.3	122	6.7	0.56	7	12
9 ^c (1)	181	15.1	41.0	41.3	1.6	1.0	112	14.0	0.64	5	28
17 ^c (0.5)	171	15.1	32.2	49.0	1.4	2.3	121	8.3	0.64	6	10
Nickel catalyst ^d											
9 ^c (1)	183	17.4	58.4	22.5	—	1.7	94	25.7	0.64	1.4	16
Reaction <i>without</i> sonifier Copper chromite catalyst ^e											
10 ^c (2)	198	14.4	23.5	54.9	—	7.2	134	—	—	—	—
240 ^f (2)	198	14.4	28.2	54.3	—	3.1	126	—	—	10	∞
Nickel catalyst ^d											
480 ^f (1)	200	16.0	51.3	30.3	—	2.4	103	18.5	0.60	1.6	20

^aBased on GC analysis.

^bCatalyst: copper chromite (1%); pressure: 115 psig; H₂ flow rate: 1 L/min.

^cProduct discharged from initial port #1.

^dCatalyst: nickel (0.025%); pressure: 115 psig; H₂ flow rate: 1 L/min.

^eCatalyst: copper chromite (1%); pressure: 500 psig; H₂ flow rate: 1 L/min.

^fProduct discharged from final port #9.

generated (to 7.2% triene) after 10 sec. Extending the reaction time to 4 min resulted in a decrease of triene from 7.5 to 3.1%. At lower pressures, the extent of hydrogenation would be still less. For nickel-catalyzed hydrogenation of soybean oil at 100 psig and 200 C without ultrasonic power, 8 min was required to reduce the triene to 2.4% and an IV of 103. Detailed results on continuous slurry hydrogenation of soybean oil at pressures to 4500 psig will be reported by Koritala et al. (9). The linoleate selectivity, K_{Lo}/K_{O1}, was about the same, 16-20, for nickel catalyst when hydrogenating with and without the application of ultrasonic energy. However, for copper chromite, the linoleate selectivity was much greater without ultrasonic energy (∞) than with it (10-28). These selectivity values are, however, comparable to those obtained with nickel catalyst.

Research is continuing to investigate the effect of hydrogenation conditions and the amount of ultrasonic energy applied on the hydrogenated product.

REFERENCES

1. El' Piner, I.E., *Ultrasound: Physical, Chemical and Biological Effects*, Consultants Bureau, New York, 1964.
2. Atkinson, G., S.K. Kor and S. Petrucci, *Proc. IEEE*, 53:1355 (1965).
3. Franklyn, G.P.A., K.D. Timmerhaus and H.S. Fogler, *AIChE J.* 13:453 (1967).
4. Suslick, K.S., *JACS* 103:7342 (1981).
5. Blitz, J., *Ultrasonics: Methods and Application*, Van Nostrand Reinhold Co., New York, 1971.
6. Boudjouk, P., and B. Han, *J. Catalysis* 79:489 (1983).
7. Koritala, S., *JAOCS* 57:293 (1980).
8. Koritala, S., J.P. Friedrich, T.L. Mounts, *JAOCS* 57:1 (1980).
9. Koritala, S., K.J. Moulton, E.N. Frankel and W.F. Kwolek, Abstract paper 270, 74th Annual meeting AOCs, Chicago, IL, *JAOCS* 60:743 (1983).

[Received February 4, 1983]