

Kinetics of Liquid Phase Hydrogenation of Cottonseed Oil with Nickel Catalysts

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The hydrogenation of cottonseed oil has been carried out in a batch reactor using both unmodified and chromia modified nickel catalysts. The process variables include chromium to nickel atomic ratio (0.00–0.35), catalyst particle size (200–400 micron), temperature (120–140°C) and pressure (5–10 bar). Chromia was found to suppress the stearate formation completely, although it retarded the overall hydrogenation activity of nickel. Its optimum content in the catalyst was found to be 0.17 Cr/Ni atomic ratio; the data corresponded to 5 hr reaction time. The kinetics of the process was tested and found to follow a first order reaction with respect to linoleate and half order with respect to hydrogen. The activation energy was found to be 11.8 kcal/mole.

The hydrogenation of vegetable oil plays an important role in the expanding production of edible fats and margarines. The hydrogenation process partially or fully saturates and isomerizes the double bonds of fatty acid moieties, and increases the melting point as well as the stability to oxidative changes of the products. Industrial hydrogenation units widely use nickel supported on silica gel as the catalyst (1). However, the details of process development in respect to catalyst modifiers (in particular) are not available in the literature.

Kinetics studies have been made by many scientists with a variety of oils, such as cottonseed, soybean, sunflower and rapeseed oil; however, the majority of these studies have dealt with cottonseed oil. Eldib and Albright (2) showed that the iodine value decreased according to first order kinetics during hydrogenation. Using this concept, many investigations were carried out by others, including Wisniak and Albright (3), Albright (4), Hashimoto *et al.* (5), Bern (6) and Marangozis *et al.* (7). Van der Plank *et al.* (8) investigated the kinetics of double bond migration during the hydrogenation of fatty oils. Gut *et al.* (9) studied the kinetics of hydrogenation of sunflower oil and found that the reaction scheme followed a dual site Langmuir-Hinshelwood mechanism.

In the present work partial hydrogenation of cottonseed oil was carried out with chromium-modified nickel catalysts. The aim of the investigation was to (i) study the effect of chromium on nickel catalyst, and (ii) determine the kinetics of the hydrogenation reaction.

EXPERIMENTAL PROCEDURES

Apparatus. The hydrogenation was carried out in a 1-liter autoclave with 620 ml of cottonseed oil in each

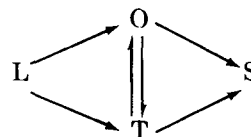
batch. Hydrogen was bubbled through the oil at a rate of 1 liter per minute, measured at the room temperature. The experiments were conducted over a temperature range of 100–140°C, catalyst particle size range of 200–400 microns and pressures of 5 and 10 bar. Further details of the procedure are available elsewhere (10).

Materials. A refined cottonseed oil was chosen for the present study. Its fatty acid composition (mole %) was palmitic 22.5, stearic 3.5, oleic 22.5 and linoleic 51.5. The catalyst was 25% nickel by weight. Chromia was used as the catalyst modifier, and its content was varied from 0.07 to 0.35 Cr/Ni atomic ratio. Silica gel acted as the catalyst support; its BET surface area was 32 m²/g. All hydrogenations were carried out at a catalyst loading of 0.1% nickel with respect to oil.

Catalyst preparation. Predetermined amounts of nickel nitrate or a mixture of nickel nitrate and chromium nitrate were dissolved in 50 ml distilled water. A known amount of silica gel was transferred to a three-necked, 250-ml flask. One neck was connected to a vacuum pump, the second was fitted with a thermometer and the third was used for charging the feed. The silica gel was degassed for about 5 min under 300 mm Hg vacuum at 60°C. Then the solution was added to the silica gel and heated to 110°C under vacuum with gentle shaking for about 30 min for evaporation of water. Thereafter, the samples were dried at 120°C for 1 hr and calcined at 450°C for 4 hr in a horizontal furnace. Finally the catalyst was reduced at 450°C by passing a hydrogen stream through it at 60 l/hr for 4 hr (11).

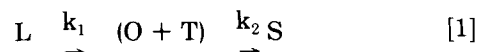
Analytical methods. The oil samples were analyzed by gas liquid chromatography (12). The triglycerides were converted into methyl esters which were analyzed on a 2 m long stainless steel column (3 mm dia.) packed with 20% DEGS on chromosorb-W. The chromatograph was fitted with a flame ionization detector. Iodine value was estimated by the Wijs method (13).

Kinetic model. Albright (14) presented the following scheme to describe the kinetics of both hydrogenation and *cis/trans* isomerization:



SCHEME 1

When *cis/trans* compositions are represented collectively, then the hydrogenation reaction can be represented as:



When a selective catalyst does not produce any stearate, then the decoupling reaction scheme for linoleate disappearance can be expressed as:

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$$-r_L = -\frac{dC_L}{dt} = k \cdot \frac{C_H^\alpha \cdot C_L}{H} \quad [2]$$

The reaction rate is assumed to be first order with respect to linoleate. Moreover, the reaction order α for hydrogen is assumed to be independent of temperature and extent of conversion.

Evaluation of rate parameters by a nonlinear regression method. The parameters k and α in the rate Eq. [2] were estimated by nonlinear regression (15). The rate expression can be conveniently rewritten as:

$$-r_L = A \exp(-E/RT) \cdot \frac{C_H^\alpha \cdot C_L}{H} \quad [3]$$

This rate expression assumes the validity of the Arrhenius equation. Furthermore, using a reference temperature T_1 (corresponding rate constant being k_1), the specific rate constant k may be represented by:

$$k = k_1 \exp\left(-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_1}\right)\right) \quad [4]$$

On substitution of this value of k , Eq. [2] becomes:

$$-r_L = k_1 \exp\left(-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_1}\right)\right) \cdot \frac{C_H^\alpha \cdot C_L}{H} \quad [5]$$

It should be noted that the concentration of hydrogen in oil, C_H , is the equilibrium solubility of hydrogen in cottonseed oil. This was estimated by the Wisniak and Albright correlation (3).

RESULTS AND DISCUSSION

Catalyst evaluation. Nickel catalysts supported on silica gel were used in the present work with and without chromia (Cr_2O_3). The nickel content of the catalyst was kept at 25% by weight on the basis of the literature (1). The content of chromia was varied between Cr/Ni atomic ratios of 0.07 and 0.35. A comparison was made

between unmodified and modified catalysts under identical reaction conditions (140°C, 5 bar, 5 hr, 0.3 mm particle size and 1200 rpm). Figure 1 presents the results obtained with the unmodified catalyst along with those obtained with modified catalyst containing the optimum Cr/Ni ratio of 0.17. The most significant point to note is that the stearate concentration increased from 3.5–46.7% with unmodified catalyst in the range of process conditions studied, while there was practically no change in the stearate content when the modified catalyst was used under the same conditions.

Effect of modifier concentration. Results with varying concentration of chromia are presented in Table 1 and Figure 2.

Chromia selectively reduced linoleate to oleate without raising stearate concentration. However, the overall reduction of iodine value was less when chromia was added to nickel. Therefore, chromia did not act as a promoter of nickel catalyst in the strict sense of the term; rather, the catalyst was modified by chromia.

The 5-hr reaction concentration of oleate attained a maximum of 52.2% at the Cr/Ni ratio of 0.17. It was lower for catalysts with higher or lower Cr/Ni ratios. This is in accordance with the role played by a promoter or modifier in catalysis. A large increase in promoter or modifier concentration results in the loss of active sites on the catalyst surface and leads to a decrease in reaction rate. Hence, the modified catalysts with Cr/Ni ratio of 0.17 were selected for further studies for evaluating the intrinsic kinetics of the process.

Effects of agitation. For both this and the next experiment (effect of particle size), a different lot of cottonseed oil was used. After 5-hr hydrogenation, its iodine value was 46.5, as opposed to 31.7, for the main oil sample. Three different stirrer speeds, 800, 1200

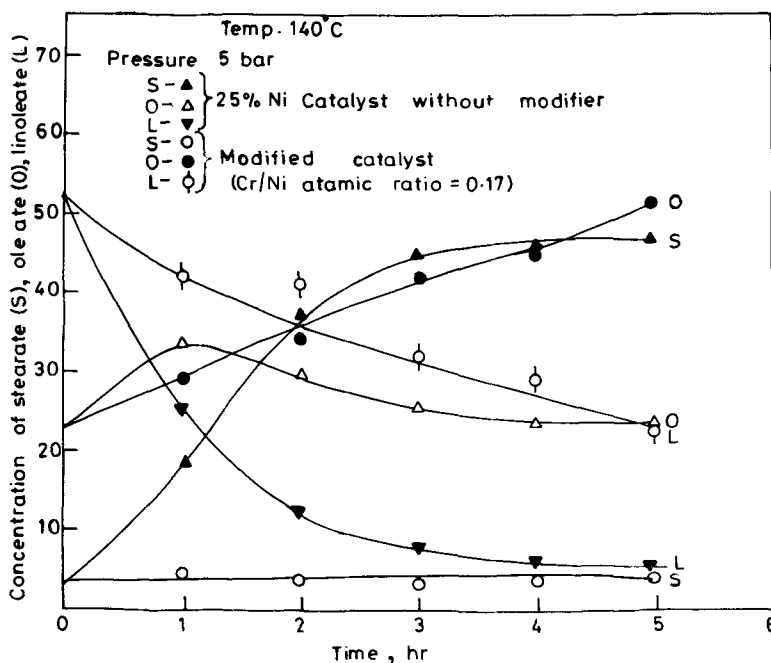


FIG. 1. Effect of modifier on product composition.

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TABLE 1

Effect of Concentration of Modifier (Temp., 140°C; Pressure, 5 bar; Time, 5 hr; Particle size, # 0.30 mm; Rpm, 1200)

| Modifier concentration, Cr/Ni atomic ratio | Composition, mole% | | | | | |
|--|--------------------|------|------|------|------|-------|
| | M | P | S | O | L | IV |
| 0.00 | 0.5 | 22.3 | 46.7 | 23.9 | 6.5 | 31.7 |
| 0.07 | 0.5 | 21.5 | 4.5 | 45.0 | 28.5 | 88.0 |
| 0.17 | 0.5 | 21.9 | 3.8 | 52.2 | 22.0 | 83.1 |
| 0.26 | 0.5 | 22.1 | 3.8 | 50.5 | 23.1 | 83.3 |
| 0.35 | 0.5 | 22.5 | 3.6 | 22.7 | 51.6 | 108.5 |

and 1500 rpm, were used with an unmodified catalyst containing 25% Ni on silica. It can be seen from Figure 3 that there was no significant change in iodine value at different speeds, which indicates that the external mass transfer resistance was negligible for the stirrer speeds employed in this investigation. For the sake of convenience, agitation was kept at 1200 rpm for the main experiments with modified catalyst.

Effect of particle size. Experiments were carried out with the unmodified catalyst at three different catalyst sizes—200, 300 and 400 microns—under identical process conditions. The effect of catalyst sizes on the extent of hydrogenation of cottonseed oil is clearly borne out in Figure 4. Iodine value was constant for the above catalyst size range. For the sake of convenience, 300 micron size was chosen as the catalyst particle size for the main experiments in this work.

Effect of temperature. As reported in the preceding sections, the mass transfer resistances were negligible under the conditions employed. Therefore, the overall process was controlled by surface reactions. The data obtained in the range of 100–140°C at 10 bar as shown in Table 2 were used to determine the intrinsic

kinetics. From this Table, linoleate conversions with time for three different temperatures were calculated. The results are shown in Figure 5, where it may be seen that the conversion of linoleate increased with temperature and attained about 85% in 5-hr reaction time at 140°C.

Effect of pressure. Between 5 bar and 10 bar pressures, the stearate concentration remained practically the same, the oleate concentration increased and linoleate concentration decreased to a much greater extent at the higher pressure. For example, after 5 hr of hydrogenation at 140°C, the oleate concentration rose from 22.5 to 64.2% at 10 bar, while at 5 bar, the rise was from 22.5 to 52.2%. The fall in linoleate concentration was from 51.5% to 8.2% at 10 bar and to 22.0% at 5 bar.

Significance of pore diffusion. It was undertaken to test the generalized Thiele modulus and the Wiesz and Hicks criteria (16).

The values of generalized Thiele modulus were calculated by the methods of Bischoff (17) and Levenspiel (18). For all temperatures these values were very much less than one, thus indicating the absence of pore diffusional resistance.

The diffusion coefficient of hydrogen in cottonseed oil was calculated from the Scheibel correlation (19). The tortuosity was taken as four, as recommended by Satterfield (20). The calculated values of $r_o^2 k / 9D_{eH}$ [Weisz and Hicks criteria (16)] are very much less than one, indicating again that pore diffusional resistance was negligible.

Rate equation. The mathematical model (Eq. [5]) for partial hydrogenation for negligible stearate formation was tested for fitting the experimental data. The rates of linoleate conversion were calculated from the graph of conversion vs time (Fig. 5). These data were used for the evaluation of the rate parameters k_1 , E and α in Eq. [5] by nonlinear regression. The reference temperature was taken as 100°C. The resultant

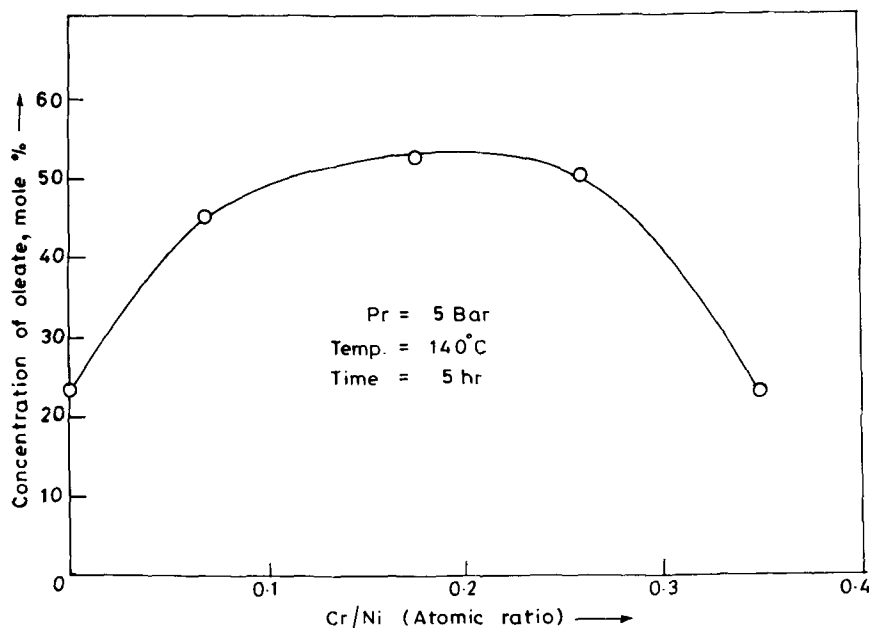


FIG. 2. Effect of modifier concentration on oleate concentration.

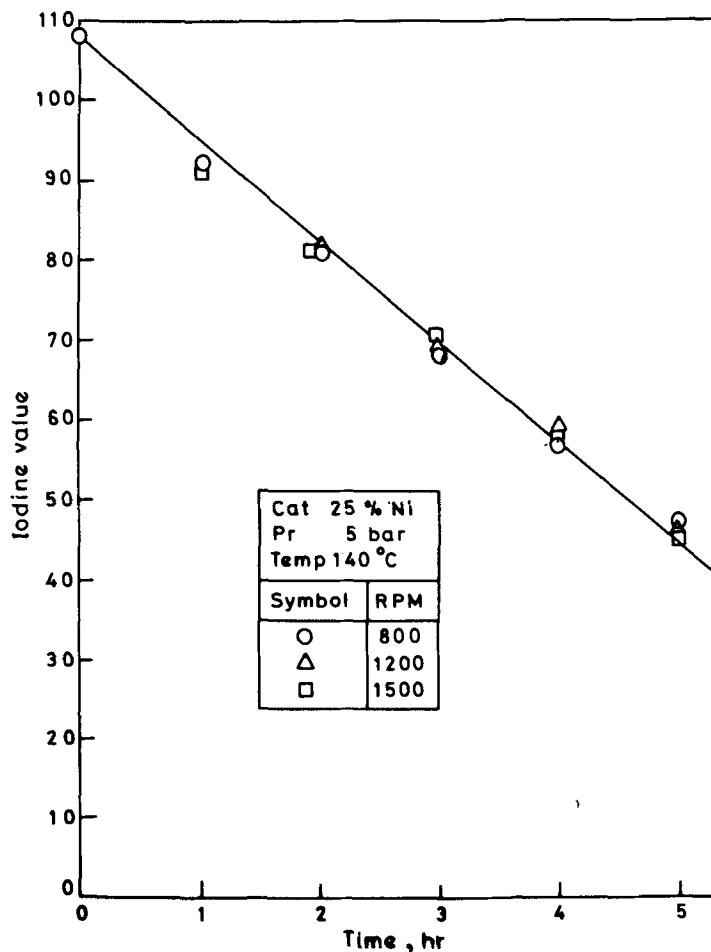


FIG. 3. Effect of agitation on degree of saturation with unmodified catalyst.

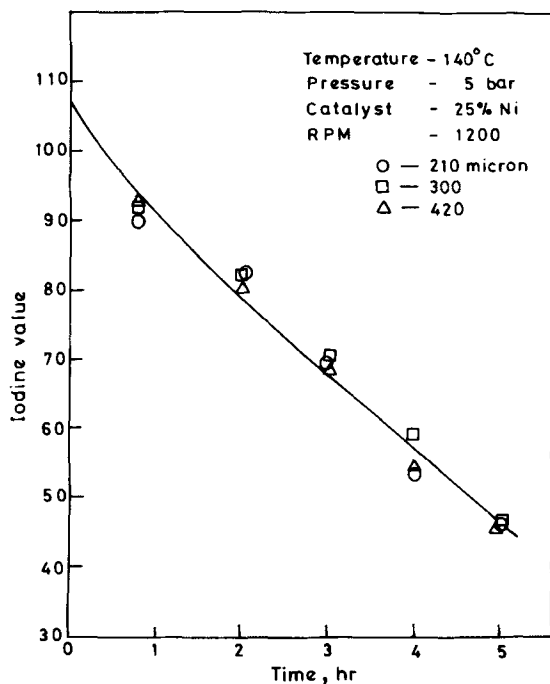


FIG. 4. Effect of particle size on degree of saturation with unmodified catalyst.

TABLE 2

Effect of Temperature (Modified catalyst; Cr/Ni = 0.17; Pressure, 10 bar)

| Temp. °C | Time, hr | Composition, mole% | | | | | |
|-------------|--------------------|--------------------|------|-----|------|------|-------|
| | | M | P | S | O | L | IV |
| 100 | Initial oil sample | 0.5 | 22.0 | 3.5 | 22.5 | 51.5 | 108.5 |
| | 1 | 0.4 | 22.8 | 3.9 | 24.8 | 48.0 | 104.3 |
| | 2 | 0.4 | 23.3 | 3.5 | 27.8 | 45.0 | 101.6 |
| | 3 | 0.5 | 22.4 | 4.0 | 30.9 | 42.0 | 101.0 |
| | 4 | 0.6 | 22.8 | 3.5 | 33.3 | 39.0 | 100.0 |
| 120 | 5 | 0.5 | 22.0 | 3.8 | 36.1 | 35.5 | 96.6 |
| | 1 | 0.5 | 22.6 | 2.9 | 30.8 | 43.1 | 103.8 |
| | 2 | 0.5 | 22.5 | 3.1 | 38.2 | 35.5 | 94.5 |
| | 3 | 0.4 | 22.3 | 3.1 | 42.5 | 31.5 | 92.6 |
| | 4 | 0.4 | 22.4 | 3.5 | 43.5 | 30.3 | 90.2 |
| 140 | 5 | 0.4 | 21.1 | 3.2 | 48.6 | 26.5 | 87.7 |
| | 1 | 0.5 | 22.7 | 3.7 | 31.4 | 41.6 | 99.1 |
| | 2 | 0.7 | 23.2 | 3.4 | 38.9 | 33.6 | 97.7 |
| | 3 | 0.5 | 22.0 | 3.6 | 48.7 | 25.1 | 85.7 |
| | 4 | 0.7 | 23.2 | 4.2 | 61.4 | 16.8 | 79.8 |
| | 5 | 0.6 | 22.8 | 4.0 | 64.2 | 8.2 | 62.8 |

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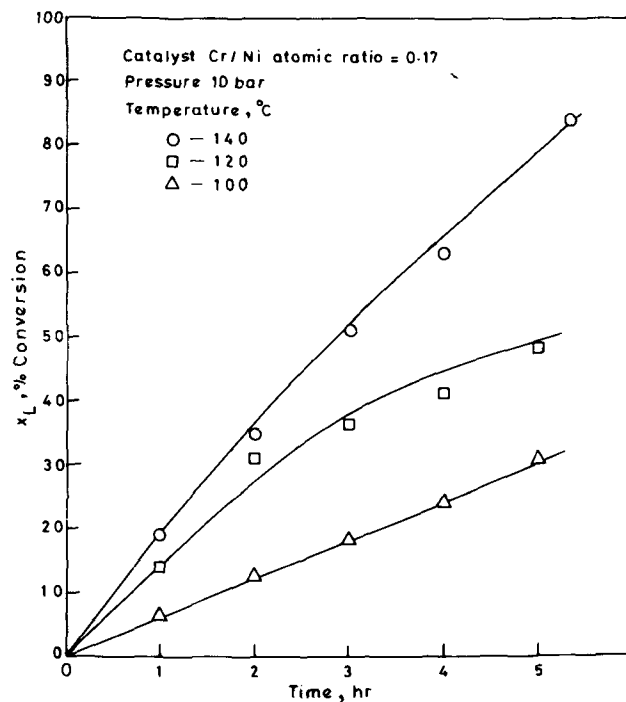


FIG. 5. Effect of temperature on linoleate conversion with modified catalyst.

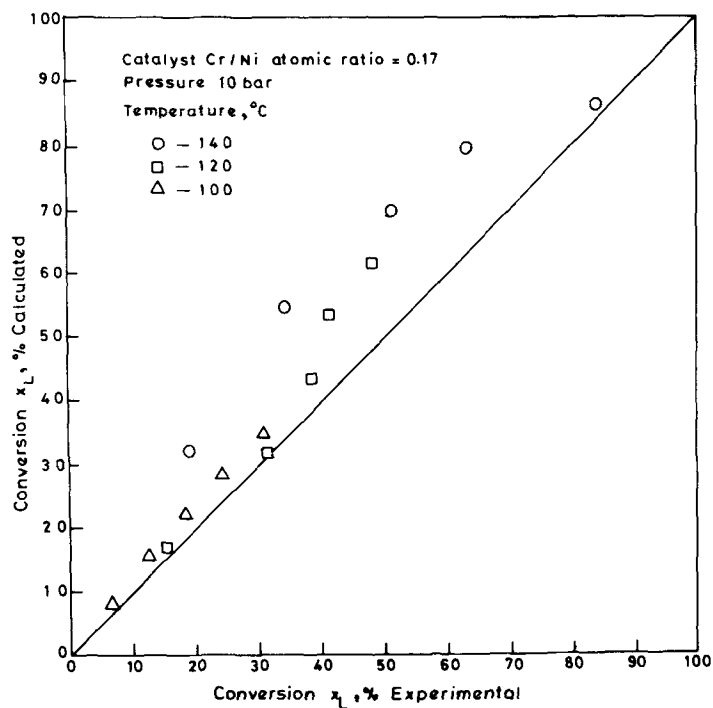


FIG. 6. Calculated vs experimental conversion of linoleate.

expression for the rate of linoleate disappearance is given below:

$$-r_L = 1.1 \times 10^2 \exp \left[-\frac{E}{R} \left(\frac{1}{T} - \frac{1}{373} \right) \right] \cdot \sqrt{C_H} \cdot C_L \quad [6]$$

The energy of activation E and Arrhenius factor are 11.8 kcal/mole and $1.95 \times 10^4 \text{ lit}^{0.5} \text{ mole}^{-0.5} \text{ hr}^{-1}$, respectively. The reaction order with respect to hydrogen is 0.5. This indicates that the hydrogen atoms are formed by dissociation of hydrogen molecules on the catalyst surface, and then these atoms react with the double bonds.

On integration of Eq. [2] and putting the value of α equal to half, the following integrated expression is derived for the conversion of linoleate:

$$-\ln(1-X_L) = k \sqrt{C_H \cdot t} \quad [7]$$

The calculated and experimental values of conversion of linoleate are plotted in Figure 6. The calculated values are higher than the experimental. The deviation is higher for the higher temperature data. The average deviation is 29.5%.

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REFERENCES

1. Allen, R.R., in "Bailey's Industrial Oil and Fat Products", edited by D. Swern, John Wiley and Sons, New York, Vol.

- 2, 4th edn., 1982, pp. 1-100.
2. Eldib, I.A., and L.F. Albright, *Ind. Eng. Chem.* 49:825 (1957).
3. Wisniak, J., and L.F. Albright, *Ibid.* 53:375 (1961).
4. Albright, L.F., *J. Am. Oil Chem. Soc.* 50:255 (1973).
5. Hashimoto, K., K. Muroyama and S. Nagata, *Ibid.* 48:291 (1971).
6. Bern, L., M. Hell and W.M. Schoon, *Ibid.* 52:391 (1975).
7. Marangozis, J., O.B. Keramides and P. George, *Ind. Eng. Chem. Process Des. Dev.* 16:361 (1977).
8. Van der Plank, P., B.G. Linsen and H.J. Van der Berg, *Proc. Fifth Eur. Second Int. Symp. on Chem. React. Eng.*, May 2-4, 1972, pp. B6-21-35.
9. Gut, G., J. Kosinka, A. Prabuki and A. Schuerch, *Chem. Eng. Sci.* 34:1051 (1979).
10. Krishnaiah, D., Ph.D. Thesis, Department of Chemical Engineering, Indian Institute of Technology, Bombay, 1985.
11. Venkateswarlu, D., (ed.), *Chem. Tech. III*, Chemical Engineering Development Centre, IIT Madras, India, 1975, pp. 4.1-4.15.
12. Anon., "Analysis by Gas Liquid Chromatography", Part 3, Bureau of Indian Standards, New Delhi, 1976.
13. Paquot, C., (ed.), "Standard Methods for the Analysis of Oils, Fats and Derivatives", Pergamon Press, Oxford, 1979, pp. 42-48.
14. Albright, L.F., *Chem. Eng.* 11:197 (1967).
15. Marquart, D.W., *J. Soc. Ind. Appl. Math.* 11:431 (1963).
16. Weisz, P.B., and J.S. Hicks, *Chem. Eng. Sci.* 17:265 (1962).
17. Bischoff, K.B., *AIChE J.* 11:351 (1965).
18. Levenspiel, O., "Chemical Reaction Engineering", Wiley Eastern Limited, New Delhi, 1978, p. 477.
19. Scheibel, E.D., *Ind. Eng. Chem.* 46:2007 (1954).
20. Satterfield, C.N., "Mass Transfer in Heterogeneous Catalysis", MIT, Cambridge, 1970, pp. 152-156.

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