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# Catalytic Hydrogenation of Methyl Laurate to Lauryl Alcohol

A method of recycling of an active long-lived catalyst may provide a continuous process for rapidly converting most fatty acid esters to alcohols

**P**RINCIPAL SOURCES of fatty alcohols and their derivatives are corresponding acids which occur as glycerides in marine, animal, and vegetable oils (23). They are produced commercially either directly from glycerides, or from simple esters of the fatty acids by one of two reductive methods—i.e., sodium-alcohol reduction or catalytic hydrogenation. Where R represents an alkyl or glyceryl group,

 $\begin{array}{l} C_{11}H_{23}CO.OR \ + \ 4Na \ + \ 3C_{2}H_{5}OH \ \rightarrow \\ C_{11}H_{23}CH_{2}OH \ + \ RONa \ + \ 3C_{2}H_{5}ONa \end{array}$ 

## $\begin{array}{l} C_{11}H_{23}CO.OR \ + \ 2H_2 \ + \ Cat. \rightarrow \\ C_{11}H_{23}CH_2OH \ + \ ROH \end{array}$

Until recently, the sodium-alcohol reduction process was the chief method for producing fatty alcohols. The original reaction, discovered by Bouveault and Blanc as early as 1903 (7) consisted of reducing lower esters of the corresponding fatty acids, using sodium metal and absolute alcohol. Because of continued improvements during the past 40 years, this method has been generally employed for synthesizing a great variety of fatty alcohols.

Commercially, however, it has certain inherent disadvantages (19) such as higher costs of the reducing agent, undesirable side reactions and consequent by-products, lower yields caused by the alkaline medium, and operational hazards and difficulties in handling metallic sodium. On the other hand, features which have made it commercially attractive are preferential reduction of the carboxyl group without much alteration in the unsaturated character of the oleic-type glycerides, and recovery of the glyceryl portion of the glyceride unchanged.

The catalytic hydrogenation method developed more recently, was the first of the commercial processes introduced in Germany about 1928 (8). This process uses a great variety of catalysts, most of which are copper chromite types with other metallic oxides and alkaline earth metals added as promoters (2, 4, 9,

<sup>1</sup> Present address, National Starch Co., Alexandria, Egypt. 16, 20, 27). Hydrogenation was carried out at  $250^{\circ}$  to  $350^{\circ}$  C. under several hundred atmospheres of hydrogen pressure, employing either the fatty glyceride, or a simple alkyl ester of the fatty acid, prepared beforehand from the glyceride by alcoholysis (10, 12, 28).

When a mild chromite catalyst such as zinc chromite (26) or copper-cadmium chromite (6) is employed under well controlled temperature conditions, hydrogenation is confined mainly to the carboxyl group, thus permitting recovery of unsaturated fatty alcohols, with a minimum reduction of oleic bonds. However, the glyceryl portion of the glyceride is partially reduced to the corresponding hydrocarbon, and where recovery of glycerol is desired, it is best to do this beforehand by an alcoholysis of the glyceride, using the resulting simple ester of the fatty acid for catalytic hydrogenation to the corresponding fatty alcohol. With continued development, the catalytic process has become competitive with sodium-alcohol reduction, and accounts for a large part of fatty alcohol production (18, 24).

Another commercial process for catalytic hydrogenation of fatty glycerides, the "lead soap process" (24), was developed shortly before War II. Here, the lead salt of the fatty acid is first prepared by saponifying the glyceride and subsequently recovering glycerol. The suspended lead soap is hydrogenated at 320° C. under a hydrogen pressure of 300 atm., without catalyst. The reaction products consist of both the fatty alcohol and the fatty alcohol ester of the fatty acid, as well as metallic lead.

Fatty alcohols are used for producing industrial synthetic detergents and emulsifying agents, which are widely used by the textile and cosmetic industries. These are prepared by reaction of the fatty alcohol with concentrated sulfuric acid or oleum and subsequent neutralization to form the corresponding sulfate and sulfonate salts. Fatty alcohols are also used for synthesizing higher alkyl quaternary ammonium compounds that have high germicidal power. In some instances, the alcohols have good properties as oil additives and are used in mixtures of certain types of lubricating oils and greases. Recently, a new use has been developed in preparing plasticizers for resins in plastic and paint compositions. For this, the fatty alcohol esters of phthalic and maleic anhydrides (17) have been most promising.

## Experimental

In the search for an industrial process for preparing fatty alcohols in general, some 35 catalytic hydrogenations of methyl laurate to lauryl alcohol (*n*dodecanol) were made to determine optimum conditions for an efficient hydrogenation rate and maximum yield of fatty alcohol. Various types of catalysts in different amounts and prepared by different methods, with and without promoters, were used. Also, a wide range of temperatures and pressures and various time periods for hydrogenation were studied.

**Hydrogenation Equipment.** A 1liter stainless steel Magne-Dash autoclave (Autoclave Engineers, Inc.) was used, consisting of a cylindrical body having an inside diameter of 3 inches, depth 9.5 inches, and a wall thickness of about 1.5 inches. The cover contained a thermocouple well for determining temperature of the contents, an inlet with attached pressure gage for hydrogen, and an opening containing a safety flange with blowout disk, set at a predetermined pressure of 7500 pounds per square inch for immediate rupture should excessive pressure develop.

Electromagnetic coils mounted on the cover provided agitation by alternately raising and dropping a stainless steel dasher plate; thus, need for a stuffing box or external moving parts is avoided. Degree of agitation could be varied from 3 cycles per second to one cycle per 10 seconds merely by changing the timer switch which provided current to energize the magnetic coils. The dasher plate traveled a vertical distance of about 2 to 3 inches, depending upon the time cycle and the number and type of disks added to it.

The autoclave was heated by means of electric strip heaters mounted in a selfcontained, well-type heater unit with an insulated jacket. The heating circuit consisted of two 1000-watt units, connected in parallel to the outlet of a variable-type transformer for proper control of the heating. A calibrated ironconstantan thermocouple, used in conjunction with a potentiometer circuit, was employed to determine the internal temperature of the autoclave.

Other necessary accessories included valves, fittings, and high pressure tubing connected to the hydrogen cylinder and blowout assembly for releasing excess gas.

**Preparation of Catalysts.** Most of the catalysts, generally of the copperchromite type, were first precipitated from suitable soluble salts as a gelatinous complex hydroxide mixture which in turn was calcined with or without impregnation upon various catalyst supports at various temperatures.

 $2Cu(NO_3)_2 + (NH_4)_2Cr_2O_7 + 4NH_4OH$  $\rightarrow 2Cu(OH)NH_4CrO_4 + 4NH_4NO_3$ 

 $2Cu(OH)NH_4CrO_4 \xrightarrow{300^{\circ}C.}$ 

 $2{\rm CuO}\,+\,{\rm Cr}_2{\rm O}_3\,+\,{\rm N}_2\,+\,5{\rm H}_2{\rm O}$ 

or  $2Cu(OH)NH_4CrO_4 \xrightarrow{500^{\circ}C.}$  $CuO + CuCrO_4 + N_2 + 5H_2O$ 

In preparing catalysts, only reagent grade chemicals of known assay were used. A typical procedure consisted of dissolving in 900 ml. of distilled water by warming to  $80^{\circ}$  C., 260 grams of copper nitrate [Cu(NO<sub>3</sub>)<sub>2</sub>.3H<sub>2</sub>O], and 31 grams of barium nitrate [Ba(NO<sub>3</sub>)<sub>2</sub>]. This was then added to a stirred solution of 151 grams of ammonium dichromate [(NH<sub>4</sub>)<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>] in 900 ml. of distilled water with 250 ml. of 28% ammonium hydroxide added.

The yellowish solution was then tested for complete precipitation by adding small amounts of ammonium hydroxide to the clear portion of the solution mixture and adjusting the pH to 6.5 when no further precipitation occurred. Too much ammonia turns the solution a deep blue color and results in lower yields of the precipitated complex.

The precipitate was then filtered, washed with two 100-ml. portions of warm distilled water, and oven-dried at 85 to 90° C. overnight. The dried precipitate was pulverized in a ball mill to a fine powder capable of passing through a 100-mesh sieve, and finally spread in a thin layer on an aluminum tray and calcined in an electric muffle furnace at  $310^\circ \pm 10^\circ$  C. for 1 to 2 hours, or until the catalyst turned completely black.

At the beginning of calcining, the reddish brown catalyst powder turned to a deep brown color when the temperature reached about  $250^{\circ}$  C. At this point decomposition set in with the liberation of much gas and the temperature rose rapidly to  $300^{\circ}$  C. In order to assure

complete decomposition, the catalyst mass was turned over several times until the whole mixture turned a deep black color without traces of brown. To assure removal of ammonia in all preparations, one half of the calcined catalyst was given a final acid leach with a 10% solution of acetic acid, followed by washes with distilled water and oven drying at  $125^{\circ}$  C.

Four different catalysts were prepared, each consisting of an unleached and an acid leached portion (Table I).

**Hydrogenation Procedure.** The methyl laurate (Eldorado Oil Works) was all of one lot having the following specifications:

Assav as methyl laurate	96.7%
Saponification No.	262
Acid No.	0.5
Boiling point at 160 mm. Hg	240° C
Sp. gr. (20°/4° C.)	0.8%
Methyl cuprate	0.9%
Methyl myristate	2.4%

Each hydrogenation charge consisted of 100 grams of methyl laurate and catalyst varying from 0.25 to 6.0 grams.

The catalyst was first dispersed by grinding to a paste with part of the methyl laurate and then stirring this well into the remainder of the ester. After charging the mixture, the autoclave was closed tightly and trapped air was removed by flushing several times with hydrogen at 200 to 300 pounds per square inch. Then the autoclave was filled with hydrogen to the desired initial pressure, using if necessary a fresh cylinder of hydrogen in order to bring the pressure above 2500 pounds per square inch. The stirrer and heating elements were then turned on and the autoclave charge was brought to the desired temperature.

After the uptake of hydrogen was completed, as noted by a reduction in the hydrogen pressure which became constant, heating was discontinued and the autoclave cooled to below  $150^{\circ}$  C. with compressed air admitted between the heating unit and the body of the autoclave. Excess hydrogen and methanol by-product vapor were removed by venting the compressed gases from the autoclave to the inside of a well ventilated hood. Remaining traces of methanol were swept out twice with hydrogen introduced at 100 to 200 pounds per square inch. After cooling to nearly room temperature, the autoclave was then opened and the product discharged to a filter for removing the catalyst. After each run the autoclave was thoroughly cleaned with methanol before using again.

Analytical Procedures. Reaction products from each run were analyzed for hydroxyl number and saponification value to determine quality of the fatty alcohol produced and the extent of conversion of the ester to alcohol.

Hydroxyl number, the milligrams of

potassium hydroxide equivalent to the hydroxyl content per 1 gram of sample, was determined using the pyridine-acetic anhydride method with minor modifications (14, 21, 22, 30). This consisted of acetylating 1 gram of the sample containing the hydroxyl compound, with a definite amount of a 25% mixture of acetic anhydride in pyridine by heating to  $100^{\circ}$  C. for 30 minutes according to the equation,

$$C_{12}H_{25}OH + (CH_{3}CO)_{2}O =$$
  
$$C_{12}H_{25}OCOCH_{3} + CH_{3}COOH$$

The excess acetic anhydride and acetic acid by-product were titrated with 0.5N potassium hydroxide to a phenolphthalein end point. A blank determination was run, and the difference calculated in terms of milligrams of potassium hydroxide per 1 gram of sample. Duplicate analyses were made and the accuracy was within  $\pm 0.5\%$  of the true value, with a maximum deviation of only  $\pm 0.2\%$ 

Saponification value, the milligrams of potassium hydroxide required to saponify 1 gram of sample, was determined by the method given in most standard analytical texts, but with slight modification (15) in amount of reagents used. Since ester content of the product in most instances was low, 4- to 6-gram samples were used, and first refluxed in 25 ml. of 0.5N alcoholic potassium hydroxide for 20 minutes to assure complete hydrolysis of the ester. Then the cooled sample was titrated for excess alkali with standard acid, using phenolphthalein as the indicator. A blank determination was made in a similar manner and the difference was calculated in terms of milligrams of potassium hydroxide consumed in saponification of 1 gram of sample.

Acid value, like saponification number, is the milligrams of potassium hydroxide required to neutralize 1 gram of sample. This determination consisted of a simple titration, to a phenolphthalein end point, of a weighed sample of the product dissolved in neutral alcohol, using 0.5Nalcoholic potassium hydroxide. In all cases, less than 0.1% acid was present in any of the products.

## **Discussion of Results**

Evaluation of Catalyst Activity. In all cases, amount of catalyst used was based on the weight of ester being hydrogenated. Typical runs with the different catalysts, using varying amounts of one catalyst were made (Table II). Contrary to results of previous investigators (4, 17), use of barium as a promoter provided little if any added activity to the catalyst, and actually resulted in slightly lower yields of alcohol. Also, contrary to previous claims, little or no increased activity occurred where catalysts were given an acid wash (1, 3, 17).

Calcining the catalyst at the higher temperature of 500° C. did not decrease activity greatly, but it did decrease the extent of hydrogenation, giving a lower yield of fatty alcohol. This was similar to results reported by Riener (25), who used a similar type of catalyst, calcined at 635° C.

Highest yields of fatty alcohol were obtained with copper-chromite type catalysts of similar composition, 2A and 4A. However, 4A, prepared from sodium chromate, showed the highest activity, giving yield of alcohol of 95.1% of theory, within 68 minutes reaction time, while 2A, prepared from ammonium chromate, gave a similar yield of 95.0% but required a reaction time of 160 minutes.

In all runs, conditions were held nearly constant, except for allowing sufficient time for completion of the hydrogenation reaction. This was indicated by the pressure decreasing to a constant minimum value-i.e., when no further hydrogen uptake occurred. Maximum yield of fatty alcohol with a minimum reaction time was obtained using 4% of catalyst. However, a similar result was also obtained employing only 2% catalyst, but 50% more reaction time. Yield for the 3% catalyst concentration was slightly lower than expected, but reaction time was shorter, indicating perhaps an incomplete hydrogenation. At higher catalyst concentrations, yield was somewhat lower, but again, the reaction time was shorter. However, that this lower yield was not caused by insufficient hydrogenation, is indicated by the small amount of ester remaining in the product. Instead, yield loss probably occurred through further hydrogenation of the alcohol to the hydrocarbon. Therefore, amounts of catalyst in excess of 4% by weight of the ester should be avoided because of overhydrogenation.

A further loss in yield of fatty alcohol occurred through an ester interchange between the lauryl alcohol product and the methyl laurate, thus forming the lauryl laurate ester. This could account for the discrepancy in material balance of some runs, where the ester, calculated as the methyl laurate, totaled less than 100% of the products to be accounted for. Since molecular weight of the lauryl ester is nearly twice that of the methyl ester, this would help to account for some losses in yield. Thus, total yield of lauryl alcohol, both free and as lauryl ester, could have been as much as 2 to 3% greater than that calculated from the hydroxyl number.

Catalyst life was determined by repeated use of the same catalyst (No. 4-A), recovered from one batch and used in the next for six runs. The product from each run was simply decanted from the catalyst and fresh ester added for the next hydrogenation. In most of these repeated runs, sustained yields of 90% or better were obtained within 15 to 30 minutes at  $300^{\circ}$  C. under 2700 pounds per square inch pressure (Table III). Thus catalyst activity is little affected with repeated use and will remain stable for long periods. Also, it has been demonstrated (29) that this type of catalyst can be regenerated by igniting at elevated temperatures to burn off residual organic matter. This could be done should activity fall appreciably after extended use.

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Long-lived catalysts are desirable and would reduce cost of preparation and reactivation when used on a large-scale basis. More important, perhaps, in a continuous hydrogenation process, is the easy separation of these catalysts from the product for recycling.

Effect of Temperature on Rate of Hydrogenation. Since this type of hydrogenation reaction is endothermic, using higher temperatures for methyl laurate should accelerate the rate of hydrogen uptake. Using 4% of the preferred catalyst (No. 4-A) and keeping the hydrogen pressure fairly constant,

## Table I. Characteristics of Hydrogenation Catalysts

Catalyst No.	Oxide Composition	Dichromate Salt	Barium Nitrate, %	Dichrom: Nitrate Mole Ratio	Leaching
1-A	Cu-Ba-Cr	$\mathbf{NH}_4$	10	1:1	None
1-B	Cu-Ba-Cr	NH4	10	1:1	10% acetic
2-A	Cu-Cr	NH4	None	1:1	None
2-B	Cu-Cr	NH4	None	1:1	10% acetic
3-A	Cu-Ba-Cr	Na	10	1:1	None
3-B	Cu-Ba-Cr	Na	10	1:1	10% acetic
4-A	Cu-Cr	Na	None	1:1.1	None
4-B	Cu-Cr	Na	None	1:1.1	10% acetic
4-C	Cu-Cr <sup>a</sup>	Na	None	1:1.1	None

<sup>a</sup> Calcined at 500° C. instead of usual 300° C.

#### Table II. Evaluation of Catalyst Activity

(Hydrogenation at 300° C. and 2500  $\pm$  300 lb. per sq. inch)

			Reaction $Time^{a}$ .	Proc	luct		
Cat.	%	Catalyst	Min. at	Sap.	-OH	%	%
No.	Catalyst	Compn.	300° C.	No.	No.	$\mathbf{Ester}^{b}$	Alcohol
1-A	4	Cu-Ba-Cr(NH <sub>4</sub> )	73	10.5	275	3.8	91.7
1-B	4	Cu-Ba-Cr(NH4) <sup>c</sup>	135	8.8	283	3.4	94.0
2-A	4	$Cu-Cr(NH_4)$	160	9.1	286	3.5	95.0
2-B	4	Cu-Cr(NH <sub>4</sub> ) <sup>c</sup>	180	7.2	279	2.9	92.7
3-A	4	Cu-Ba-Cr(Na)	93	12.1	279	4.6	92.7
3-B	4	Cu-Ba-Cr(Na)°	55	12.1	270	4.6	89.8
4-A	1/4	Cu-Cr(Na)	65	137.0	132	52.9	43.7
	1/2	Cu-Cr(Na)	57	17.1	245	6.9	81.4
	1	Cu-Cr(Na)	92	15.5	260	5.9	86.5
	2	Cu-Cr(Na)	92	12.1	289	4.6	96.0
	3	Cu-Cr(Na)	32	18.5	264	7.1	87.8
	4	Cu-Cr(Na)	68	8.2	286	3.1	95.1
	6	Cu-Cr(Na)	27	9.0	268	3.5	89.0
4-B	4	Cu-Cr(Na)°	60	8.7	285	3.3	94.7
4-C	4	$Cu-Cr(Na)^d$	34	12.8	273	4.9	90.0
<sup>a</sup> Until	hydrogen p	ressure reduced to	constant va	alue.			

<sup>b</sup> As methyl laurate.

Acid washed.

<sup>d</sup> Calcined at 500° C.

#### Table III. Evaluation of Catalyst Life

(Hydrogenation conditions, 4% of catalyst 4-A at 300° C. and 2700 lb. per square inch hydrogen

		1	pressure)				
Total No. of Batch Time		${f Reaction}\ {f Time}^a {f at}$	Sapon.	Sapon. Hvdroxyl.		Products, %	
Batches	Min.	300° C.	No.	No.	$\operatorname{Ester}^{b}$	Alcohol	
1	75	15	16.5	271	6.3	90.0	
2	100	30	17.7	270	6.8	89.9	
3	180	12	14.4	272	5.5	90.3	
4	180	17	14.4	266	5.5	88.5	
5	105	38	10.5	279	4.0	92.6	
6	105	34	12.8	273	4.9	90.7	
Av.	124	24	14.4	270	5.5	90.3	
Total	745	146	••		••	••	
<sup>a</sup> Until l <sup>b</sup> As me	ydrogen pressure thyl laurate.	decreased to co	onstant valu	e.			



three hydrogenations were made at maximum temperatures of 250°, 300°, and 370° C. Time for complete hydrogenation was measured by the time required for hydrogen pressure to reduce to a constant value (Table IV). At the lower temperature of 250° C., reaction time was 68 minutes with less than one third of the ester hydrogenated to the alcohol. At 300° C, the reaction time was also 68 minutes, but over 95% of the ester was hydrogenated. At the higher temperature of 570° C., however, the reaction was complete in 20 minutes with little of the ester left unchanged. However, extended hydrogenation reduced 30% of the fatty alcohol product to the hydrocarbon. Thus, optimum temperature for rapid hydrogenation and maximum vield is about 300° C.

Hydrogenation rate was measured under similar conditions at the optimum temperature of 300° C., using 4% of the preferred catalyst No. 4-A under 2800 pounds per square inch initial hydrogen pressure. Samples of the chilled reaction mixture were withdrawn at definite intervals for determining ester and alcohol content. When the reaction mixture reached the desired optimum reaction temperature of 300° C., nearly one half of the ester had been hydrogenated (Figure 1). After 5 minutes at 300° C., over three fourths of the ester had been converted to alcohol and within 15 minutes, 90% of the reaction was complete. Further heating for 70 minutes at 300° C. failed to increase the yield of alcohol much above 95%, probably because some alcohol was further reduced to the hydrocarbon.

Effect of Pressure on Rate of Hydrogenation. In this work, hydrogen from cylinders was used, and no compressor was available for obtaining pressures much above 3000 pounds per square inch. However, results may be extrapolated to higher pressures within the range of 300 to 500 atm. available commercially for such hydrogenations. Using different amounts of catalyst 4-A at a 300° C., but under varying starting pressures of 2400 to 3200 pounds per square inch, hydrogenation was permitted to proceed until the reduction in pressure reached a constant value. The results (Table V) definitely indicate the advantages expected from employing higher pressures.

At the lower 2% catalyst concentration, a 10% increase in hydrogen pressure, although requiring three times the reaction time, gave a 10% increase in yield of fatty alcohol. Likewise when using 3% of catalyst, this increase in pressure gave more than a 10% increase in yield with about the same reaction time. At the optimum catalyst concentration of 4%, the effect of pressure within the range studied was not so pronounced. A 35% increase in hydrogen pressure from 2360 to 3200 pounds per square inch increased yield only 7%. However, at 2800 pounds per square inch and twice the reaction time, yield of fatty alcohol was greater than at the higher pressure.

Extrapolating these results on effect of pressure indicates that maximum yields approaching 100%, could be obtained at 300° C. under a maximum pressure of about 4500 pounds per square inch within a reaction time of about 20 minutes or less.

Effect of Agitation on Rate of Hydrogenation. Because of the heterogeneous character of the hydrogenation reaction which uses a mixture of hydrogen gas, liquid ester, and solid catalyst, agitation is an important factor, particularly for large-scale production. Most previous investigators used a rocking type of autoclave which, compared to the more vigorous agitation of the magneticstirred autoclave, gave minimum agitation. In the magnetic apparatus, degree of agitation could also be varied by changing the time cycle of the current to the magnet. Although catalysts, temperatures, pressures, as well as the extent of agitation, were different, it is interesting to compare the results of this research with that of the other investigators (Table VI) who used lower temperatures, but with one exception, higher pressures. Instead of methyl laurate,

3.1

4.9

95.0

61.5

## Table IV. Effect of Temperature on Extent of Hydrogenation

286

184.5

(Conditio	ns, 4% of catalyst 4	4-A at 2800 lb.	per sq. inch init	ial hydrogen j	pressure)
Reaction Reaction Temp., Time <sup>a</sup> , Min.	Sapon.	Hydroxyl	Produ	1ct, %	
° C.	at 300° C.	No.	No.	Ester <sup>b</sup>	Alcohol
250	68	230	91	65.7	30.3

8.2

13.5

<sup>a</sup> Until pressure reduced to constant value. <sup>b</sup> As methyl laurate.

68

20

As methyl laurate.

300

370

## Table V. Effect of Pressure on Rate of Hydrogenation

(Conditions, different amounts of No. 4-A catalyst at 300° C. under varying hydrogen pressure)

% Pressure.		Time. Min.	Sapon.	Hvdroxvl	Iydroxyl Product, %		
Catalyst	Lb./Sq. In.	at 300° C. <sup>a</sup>	No.	No.	$\overline{\mathrm{Ester}^b}$	Alcohol	
2	2750	32	20.3	264	7.8	87.1	
2	3050	92	12.1	289	4.6	96.0	
3	2600	40	26.6	237	10.1	78.8	
3	2850	32	18.5	264	7.1	87.2	
4	2360	47	15.0	263	5.9	87.5	
4	2800	15	16.5	271	6.3	90.0	
4	2800	68	8.2	286	3.1	95.0	
4	3200	38	9.8	281	3.7	93.5	

<sup>a</sup> Until hydrogen pressure decreased to constant value. <sup>b</sup> As methyl laurate.

## Table VI. Agitation Factor in the Hydrogenation Reaction

(Comparison of result from rocking vs. Magne-Dash autoclaves)

				Reaction Conditions			Fatty
Investigator	Starting Material	Catalyst Type	Cat., %	° C.	Press., Lb./Sq. In.	Time	Alcohol, %
		Rockin	g Autocla	ive			
Adkins	Ethyl laurate	Cu-CrBa <sup>a</sup> Cu-CrBa <sup>a</sup> Cu-CrBa <sup>a</sup>	7 10 10	250 250 250 250	3280 1600 3200	240 420 60	97 100 100
Riener	Methyl laurate	Cu-Cr Cu-Cr Cu-Cr	2.5 2.5	275 275 275	3000 3000 3700	120 120	92 88
Guyer	Lauric acid	Cu-Cr-Co	5 1-1-1-1-	-1	3700	90	91
Authors, run No.	Methyl laurate	Cu-Cr	asn Auto	ciave			
12	1		2	300	2850	92	96
5			4	300	2640	68	95
20			4	300	2650	15	9 <b>0</b>
16			4	300	2990	38	93
<sup>a</sup> Acid washe	d after calcining.						

some used ethyl laurate or lauric acid (13). The main difference, however, is in the type and extent of agitation.

With one exception, hydrogenations in the magnetically stirred autoclave were much faster than in the rockingtype. A good comparison where conditions were similar, is that of Riener and run 12 of this investigation where 2%catalyst was employed. The rocking autoclave required 120 minutes for a 92% yield of fatty alcohol at 275° C. and 3000 pounds per square inch, whereas the magnetic autoclave took only 92 minutes for a 96% yield of alcohol at 300° C. and 2850 pounds per square inch. Similar-type catalysts were used. The higher rate obtained with magnetic equipment was caused by better agitation. Reciprocating action of the magnetic stirrer caused better dispersion of hydrogen within the liquid and better contact with the well-distributed catalyst. This is in agreement with the opinion of others (5), who have found agitation to be most important factor for heterogeneous hydrogenation.

## **Summary and Conclusions**

This research has shown effects of type, amount, and method of preparing catalysts, and also temperature, pressure, and degree of agitation on rate and extent of hydrogenation of methyl laurate to lauryl alcohol. Using a 4% quantity of a copper-chromite type catalyst based upon the weight of ester, and temperatures of  $300^{\circ} \pm 10^{\circ}$  C. under hydrogen pressures of 2600 to 3000 pounds per square inch, better than a 90% yield of free fatty alcohol was obtained within 15 to 20 minutes. The catalyst had long life and was used several times without apparent loss of activity. With excessive amounts of catalyst, particularly

under prolonged hydrogenation times, losses in yield of fatty alcohol occurred because of further reduction to the hydrocarbon.

Because of the high activity and sturdy character of the catalyst, a continuous hydrogenation process could be developed, provided good agitation is maintained for proper suspension of the catalyst. Such a continuous process would be economical and adaptable for commercial scale. Hydrogenation would be carried out by slurrying a 4% quantity of the catalyst in the ester at high velocities, passing the mixture through a heat exchanger for heating to 250° C., then sparging with hydrogen gas under 4500 to 5000 pounds per square inch pressure, and to complete the reaction, passing the mixture through a tubular type autoclave for further heating to temperatures approaching 300° C.

Under these conditions a yield of 90 to 95% free fatty alcohol could be obtained, along with the remainder of the ester present in the product, either as the original methyl laurate or the lauryl laurate from ester interchange. After filtering off the catalyst for recycling, the free fatty alcohol could be recovered by a high vacuum distillation and the still residues, consisting of laurate esters, recirculated to the process for further hydrogenation. After many recyclings of the catalyst, when its activity has been decreased appreciably, a new lot of catalyst could be substituted, while the used catalyst was being regenerated by calcining at 300° to 350° C. for 30 minutes.

Under much the same conditions as established in this research for the optimum hydrogenation of methyl laurate to produce lauryl alcohol, many other fatty acid esters could be similarly reduced to produce the corresponding fatty alcohols.

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