TABLE IV

Effect of Influent Concentration on Effluent Level

Nonionic	Level in plant effluent Influent: 5 mg/L	Influent: 25 mg/L
7 EO	0.14	0.15
11 EO	0.15	0.10
15 EO	0.21	0.31
20 EO	0.34	0.62
Control plant (sewage only)	0.33	0.11

TABLE V

Levels of Nonionic on Activated Sludge (Influent Concentration = 25 mg/L)

Nonionic	% Nonionic on dried solids
7 EO	0.28
11 EO	0.29
15 EO	0.24
20 EO	0.25
Control plant	0.29

TABLE VI

Polyethylene Glycol Levels in Plant Effluents

Nonionic	Influent "PEG" (mg/L)	Effluent "PEG" (mg/L)	% Removal
11 EO	19.8	0.77	96.0
15 EO	20.9	2.61	88.0
20 EO	21.8	2.45	89.0

The above discussion refers only to the levels of primary biodegradation since, throughout, the analysis was made using the Wickbold method which only measures intact nonionic. To obtain some indication of the level of ultimate biodegradation, the polyglycol intermediates in the plant effluents were determined by the HBr fission method described by Tobin et al. (3). This technique determines the total -$OCH_2 \cdot CH_2$- functional groups present in the sample. The results obtained are given in Table VI.

The results clearly demonstrate that a large proportion of the PEG-like intermediates are removed during treatment and show that alcohol ethoxylates undergo extensive ultimate biodegradation during sewage treatment.

In contrast, Tobin et al. (3) found only ca. 25% ' PEG ' degradation when testing Dobanol 9E0 in the OECD confirmatory test. The rather low activity of sludges grown on synthetic wastes compared with the highly active biomass produced from domestic sewage is the most probable explanation for the discrepancy.

ACKNOWLEDGMENTS

The analysis for nonionics in plant samples was done by J. Waters and J.T. Garrigan. T.R. Williams provided technical assistance.

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Manufacture of Fatty Alcohols Based on Natural Fats and Oils

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ABSTRACT

The present worldwide capacity of fatty alcohols is ca. 1.0 million metric tons per year. About 60% of this capacity is based on petrochemical feedstocks, 40% on natural fats and oils. Three basic dominating commercial-scale processes are used to manufacture fatty alcohols: the Ziegler process and the Oxo synthesis starting from petrochemical feedstocks, and the high-pressure hydrogenation of natural fatty acids and esters. Basically, the high-pressure hydrogenation can be used with triglycerides, fatty acids or fatty acid esters as feedstock. The direct hydrogenation of fats and oils has not been developed to a commercial-scale process, mainly because it was not possible to prevent decomposition of the valuable byproduct glycerol. Conversion of fatty acids into fatty alcohols by catalytic hydrogenation without preesterification requires corrosion-resistant materials of construction and acid-resistant catalysts. Required reaction temperatures are higher, resulting in a higher hydrocarbon content. The majority of fatty alcohol plants based on natural fats and oils use methyl esters as feedstock. These can be made either by esterification of fatty acids or by-transesterification of triglycerides. For catalytic high-pressure hydrogenation of methyl esters to fatty alcohols, several process options have been developed. The bawic distinguishing feature is the catalyst application either in a fixed bed arrangement or suspended in the methyl ester feed.

INTRODUCTION

Fatty alcohols, particularly the detergent range C_{12} and higher alcohols, have become an important basic material for a host of derivatives and applications.

Today, in the Western hemisphere, the commercial production of fatty alcohols is based on three different process alternatives: the high-pressure hydrogenation of fatty acids and esters, the Ziegler synthesis, and the Oxo synthesis.

The Ziegler and Oxo processes start from petrochemical feedstocks producing synthetic alcohols, whereas natural fats and oils are the raw materials for the hydrogenation of fatty acids and esters to natural alcohols (1).

The present world capacity of natural and synthetic fatty alcohols is ca. 1.0 million metric tons/year (Table I). A regional breakdown of the world capacity into natural and synthetic fatty alcohols shows that in the USA the bulk of fatty alcohols is of petrochemical origin, whereas in Europe more than 60% of the total volume is made from natural fats and oils. Worldwide, ca. 60% of the fatty alcohol capacity is based on petrochemical feedstocks and

TABLE I

World Capacity 1983 – Natural and Synthetic Fatty Alcohols

	Natural	Synthetic
	(1,000 metric tons)	
Europe	220	130
USA	130	400
Asia	60	50
Total	410	580

ca. 40% on natural fats and oils.

The actual production volume is estimated to be of the order of 700,000 metric tons/year, corresponding to an overall capacity utilization of ca. 70%.

Process Alternatives

The commercial production of natural fatty alcohols started about 50 years ago, but continuous technological development improved the economy of this process significantly.

Tremendous progress has been made, particularly to increase the activity, selectivity and life of the catalyst systems, to reduce the energy consumption, and to install automatic computer systems to run at optimum efficiency with a minimum of manpower.

All commercial process variations for the manufacture of natural fatty alcohols start with fatty triglycerides as raw material. Primary feedstocks for the C_{12}-C_{14} range are coconut and palm kernel oil, and for C_{16}-C_{18} alcohols technical grades of tallow and palm oil are used.

A great variety of special alcohols is readily available by selection of appropriate starting oils, e.g., behenyl and erucyl alcohol from rapeseed oil, hydroxy-stearyl alcohol from castor oil, and a broad range of unsaturated alcohols with iodine values up to 170 from linseed oil.

Figure 1 shows the various routes from natural fats and oils to fatty alcohols.

Theoretically, the simplest way to convert fats and oils to fatty alcohols is the direct hydrogenation of triglycerides. This one-step process would save the manufacture of intermediates like fatty acids or methyl esters. The catalytic hydrogenolysis of triglycerides is basically feasible, but has a major drawback. The reaction conditions which have to be employed with the catalysts so far known are so severe that the valuable byproduct glycerine undergoes further hydrogenation to a mixture of propylene glycols and propyl alcohol. Since savings in capital investment cannot make up for higher hydrogen and catalyst consumption and the loss of the valuable byproduct glycerine, this route is not practiced on a commercial scale.

Another option is the splitting of fats and oils into fatty acids and glycerine and subsequent hydrogenation of the fatty acids to fatty alcohols. The direct hydrogenation of fatty acids in the absence of an alcohol component for pre-esterification is connected with some specific requirements due to the acidic medium. Most of the equipment has to be made of corrosion-resistant material; the high-pressure part has to be designed for a higher temperature and pressure than for the methyl ester route; and the catalyst has to be acid-resistant.

The hydrogenation of fatty acids is basically feasible with a copper chromite catalyst of the Adkins type, but the reduction of the carboxyl group requires temperatures of ca. 300 C, i.e., ca. 50-100 C higher than necessary for the hydrogenation of methyl esters. These more rigorous reaction conditions lead to a certain amount of overhydrogenation of the already formed fatty alcohol, resulting in a higher percentage of hydrocarbons. This is particularly the case when a broad cut of fatty acids is used as feedstock.

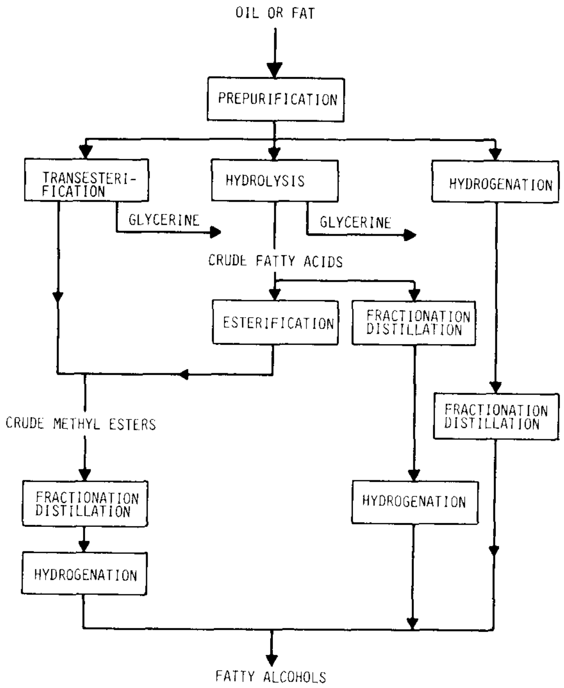

FIG. 1. Manufacturing routes of fatty alcohols from natural fats and oils.

The formation of hydrocarbons means a drop in overall yield, since they cannot be recycled into the process. The hydrogenation catalyst has to be absolutely acid-resistant since otherwise soap formation would take place, entailing a higher catalyst consumption and additional purification and rework steps. The acid-resistant copper chromite type is rather expensive and susceptible to poisoning. Thus it has a short useful life, and – a major drawback – allows only comparatively low throughput rates. This low space-time yield requires significantly larger reactor volumes than the methyl ester hydrogenation.

Last not least, there are some open questions regarding the long-term behavior and corrosion-resistance of stainless steel types continuously exposed to fatty acids at a temperature of ca. 300 C. To my knowledge, it is because of these disadvantages that the direct hydrogenation of fatty acids is not used on a large commercial scale.

Lurgi (2) has developed a hydrogenation process which allows the use of fatty acids as feedstock without previous esterification in a separate unit. Lurgi characterizes this suspension process in this way: that by recirculating fatty alcohol in a first step, an "in situ" esterification takes place to convert the fatty acid into a wax ester. The second step – the hydrogenation of this wax ester – occurs simultaneously in the same reactor. This means that the process actually is not a direct hydrogenation of a fatty acid, but the hydrogenolysis of an ester.

Methyl Ester Preparation

As a result of the problems encountered in the direct hydrogenation of fatty acids, low-molecular-weight esters of fatty acids, preferably methyl esters, have become the primary feedstock. Today the bulk of natural fatty alcohols is manufactured via the methyl ester route. Methyl esters of fatty acids can be made either by esterification of fatty acids or transesterification of fat triglycerides.

The esterification can be done batchwise under pressure at temperatures of ca. 200-250 C. Since the esterification is an equilibrium reaction, the reaction water has to be removed continuously to obtain a high ester yield.

A favorable process option is the continuous esterification in a countercurrent reaction column. Henkel has developed a process technology based on the principle of an esterification reaction with a simultaneous absorption of superheated methanol vapor and desorption of the reaction water (Fig. 2) (3). The principle of this process is an esterification reaction with a simultaneous absorption of superheated methanol vapor and desorption of the reaction water.

Preheated fatty acid containing an alkaline catalyst is fed into a double bubble plate distillation column from the top, countercurrent to methanol that enters the column from the bottom. The reaction is carried out at a pressure of ca. 10 bar and a temperature of 240 C. Excess methanol can be kept significantly lower than in the batch esterification. The batch process under pressure requires a molar ratio of methanol to fatty acid of 3-4:1, whereas for the continuous process a molar ratio of 1.5:1 is sufficient. The excess methanol leaves the column at the top together with water formed during the reaction (methanol/water = 50:50 weight %), the methyl ester is taken off at the bottom and, after passing a flash vessel to remove traces of methanol, enters a distillation unit. The methyl ester leaving the flash vessel has an acid value of down to 0.5 and does not require a refining step. The methyl ester is separated from the catalyst containing residue by topping off under vacuum. The methanol is purified by rectification and is reused as starting material.

The esterification is a preferential method for esters from specific fatty acids, which no longer represent the original composition of a natural fat, e.g., by separation into an olein and a stearin fraction. The continuous esterification process in a reaction column is superior to the batch process, in that the same high yield can be obtained in a much shorter dwell time and with a substantially lower excess of methanol.

The predominant process for the manufacture of methyl esters is the transesterification of fats and oils with methanol. The ester interchange, i.e., the replacement of the alcohol component glycerine by methanol takes place

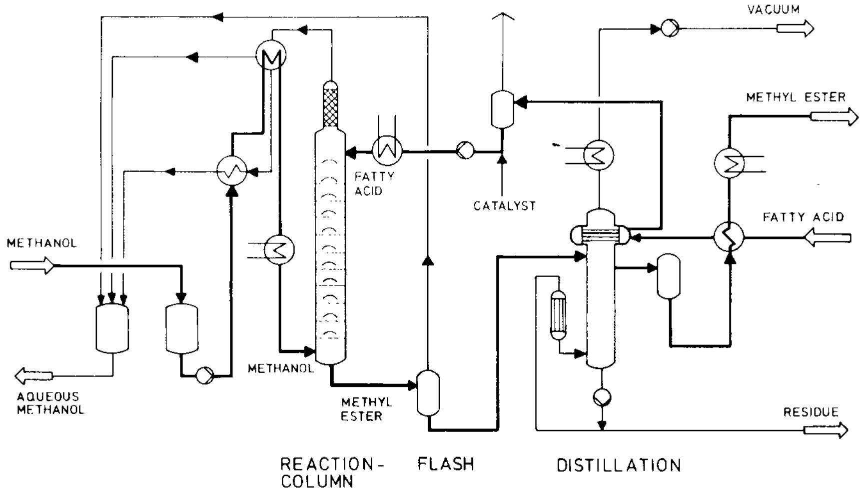

FIG. 2. Manufacture of fatty acid methyl esters by esterification.

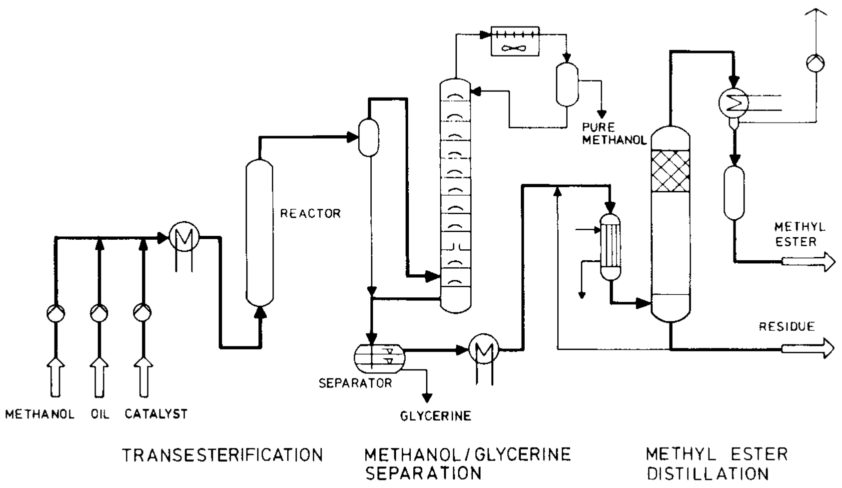

FIG. 3. Manufacture of fatty acid methyl esters by transesterification.

quite easily at low temperatures of ca. 50-70 C and under atmospheric pressure with an excess of methanol and in the presence of alkaline catalyst. After the reaction mixture has been allowed to settle, the lower glycerine layer is separated and the remaining methyl ester can be further processed.

These mild reaction conditions, however, require a preneutralization of the fat by means of e.g., alkali refining, steam distillation of preesterification of free fatty acids. The removal of free fatty acids (FFA) is not required if the transesterification is carried out under pressure, e.g., at 90 bar and at a higher temperature, e.g., at 240 C. Under these conditions, even inferior grades of fats and oils with a high FFA content can be converted into methyl esters without preneutralization, since a simultaneous esterification takes place.

Figure 3 shows the process flow diagram of a continuous transesterification unit designed for higher pressure and temperature. Unrefined oil, methanol – in an excess of several moles – and an alkaline catalyst are preheated to 240 C and are fed in parallel flow into the bottom of the reactor by metering pumps. After flashing off the bulk of the excess methanol, the reaction mixture enters a separator, in which settling into an upper layer containing the methyl ester and a lower layer consisting of the glycerine is allowed. In a bubble tray column with reflux, pure methanol is topped off and then recycled into the transesterification step. The bottom containing methyl ester and glycerine is combined with the material in the separator. The glycerine with a purity of more than 90% is removed from the ester process, and the methyl ester is transferred to a subsequent vacuum distillation. According to fatty alcohol chain distribution requirements, a simple overhead distillation or a rectification into special cuts may be applied.

The transesterification reaction under atmospheric pressure does not require pressure vessels, resulting in lower capital investment, and the excess of methanol can be kept lower than in the pressure process.

The amount of aqueous methanol to be reworked for recycling has a significant impact on the economics because of energy costs. On the other hand, a removal of free fatty acids is mandatory for the process under atmospheric pressure, whereas the transesterification under pressure allows the use of inferior grades of oil with a high FFA content without previous treatment.

High-Pressure Hydrogenation

Fatty acids or their esters are converted into fatty alcohols by high-pressure hydrogenation in the presence of heterogeneous catalysts. There are several approaches to classify the various process alternatives, depending on which feature one wants to emphasize. Depending on the form and application of the catalyst, the hydrogenation methods can be divided into suspension and fixed bed processes.

Figure 4 shows a simplified process flow diagram of a suspension hydrogenation. Fatty acid methyl ester and hydrogen are preheated separately and fed into the reactor from the bottom. The catalyst, at least 2% copper chromite powder suspended in methyl ester, is added by a metering pump. The vertical reactor is tubular and contains no packing. The hydrogenation is accomplished at ca. 250-300 bar and 250-300 C. The ester throughput per hour is in the order of magnitude of the reactor volume. Ca. 20 moles of hydrogen per mole of ester are fed into the reactor serving not only as reducing agent but also as means of agitation. The inlet temperature depends upon the degree of unsaturation of the fatty carbon chain. Since the hydrogenation both of the carbonyl group and the carbon double bonds is exothermic, the reaction of higher unsaturated esters is started at the lower end of the abovementioned temperature range, for, with increasing temperature, undesired side reactions like formation of hydrocarbons are favored.

The reaction mixture is cooled and separated into liquid and gaseous phases. The gas, mainly hydrogen, is recycled and the fatty alcohol/methanol mixture is expanded into a methanol stripping unit. After removal of the methanol the catalyst is filtered off. The crude fatty alcohol still contains 2-5% ester which can be removed by addition of alkali to form soap which remains in the bottom of the subsequent distillation. Due to overhydrogenation of the fatty alcohol, up to 2-3% hydrocarbons are formed, lowering the overall yield significantly. Even with recycling, the catalyst consumption is in the range of 0.5-0.7%.

Since with the use of copper chromite as catalyst, carbon double bonds also are hydrogenated, only saturated fatty alcohols can be obtained, no matter which methyl ester is used as feedstock.

Basically, the suspension process is also applicable to the hydrogenation of fatty acids to fatty alcohols, provided that the equipment in touch with the fatty acid is made

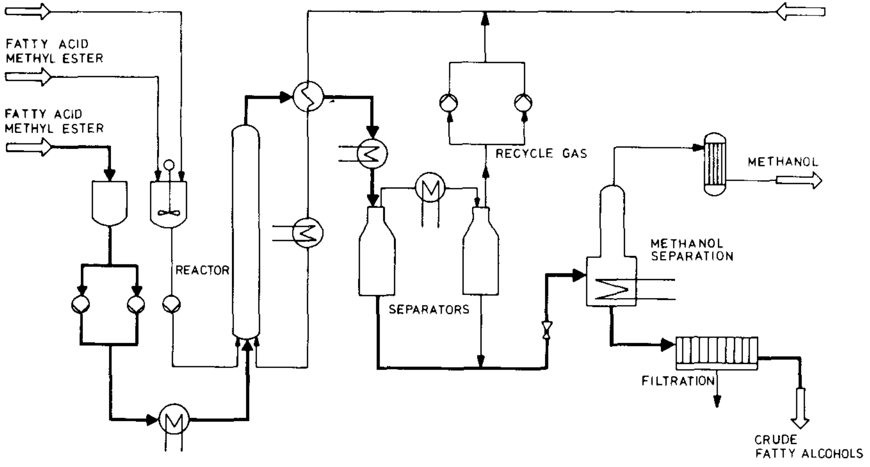

FIG. 4. High-pressure hydrogenation of fatty acid methyl esters – suspension process.

of stainless steel, and the catalyst used is acid-resistant, such as the Adkins-type copper chromite.

Significantly different from the suspension technology are process modifications based on a fixed bed catalyst system. Depending on whether the organic feed passes through the catalyst bed mainly vaporized or in a liquid state, the terms vapor phase or trickle hydrogenation are in use.

Since the state of aggregation of the reaction mixture depends on a variety of parameters such as the carbon chain length distribution of the organic feed, the amount of recycle gas, temperature and pressure conditions, and the optional addition of substances to aid in vaporization, this differentiation is not very clearly defined. Preferably, one distinguishes between the fixed bed processes by the kind of catalyst used, either compact pelletized or supported catalysts on a carrier. In the process in which a massive catalyst is employed (Fig. 5), a part of the organic feed is vaporized in an excess of 20-50 moles of hydrogen, and passed over the fixed bed catalyst. The hydrogenation is accomplished at a pressure of 200-300 bar and a temperature of 200-250 C. The methyl ester is mixed with fresh and recycled high-pressure hydrogen and heated up by heat interchange with the reaction mixture leaving the reactor. The feed is brought up to process temperature by a peak heater and enters one or several reactors from the top. The mainly vaporized material passes over the fixed catalyst bed.

In the case of manufacturing saturated fatty alcohols, the compact pelletized catalyst consists of a blend of metal oxides containing copper, e.g., copper/zinc oxide. Since the reduced form of this catalyst is pyrophoric, the activation by reduction is usually performed in the reactor. The copper/zinc catalyst is not acid-resistant and consequently not suitable for the hydrogenation of fatty acids.

If a special catalyst containing zinc is used at somewhat higher temperatures, the carbon double bonds of unsaturated fatty acid methyl esters remain unchanged, i.e., unsaturated esters can be converted into unsaturated fatty alcohols. There exist catalysts of such high selectivity that, depending on the degree of unsaturation of the ester, even highly unsaturated fatty alcohols with iodine values up to 170 can be manufactured.

After leaving the reactor, the reaction mixture is cooled and is separated into liquid and gaseous phases in a separator. The gaseous phase consisting mainly of excess hydrogen is recycled and the liquid product stream is expanded into a flash tank in which methanol is stripped from the fatty alcohol. The fatty alcohols do not require further purification. If, however, narrow cuts are desired, and a fractionation has not already been made with the methyl esters, the fatty alcohols may be fractionated in an appropriate rectification unit.

The vapor phase process conditions are comparatively mild. The high amount of recirculated gas provides fast removal of the heat of reaction, keeping side reactions such as hydrocarbon formation at a very low level. The overall yield of fatty alcohol is ca. 99%, with a content of hydrocarbons and nonhydrogenated ester not exceeding 1.0%. The catalyst consumption is below 0.3%.

The fixed bed process in which a supported catalyst is employed is basically carried out in about the same unit as used for massive catalysts. Also, the reaction conditions are similar to those for compact catalysts.

The most distinguishing feature is that the organic feed trickles down over the fixed catalyst bed in a liquid state. The molar excess of hydrogen and therewith the amount of recycled gas is considerably lower than in the process with compact catalysts. Because of the liquid state of the feed, the catalyst has to be of a high mechanical stability; therefore, supported catalysts like 20-40% copper chromite on a silica gel carrier are used. This high mechanical stability of the supported catalyst allows also the hydrogenation of materials not easily volatilized, like wax esters.

The fatty alcohols from this process are of the same high quality as achieved with massive catalysts, particularly with regard to the low hydrocarbon content. The specific catalyst consumption can be kept down to ca. 0.3%.

Since the specific throughput rate, i.e., the space-time yield, is higher with massive catalysts, plants using carrier catalysts require larger high pressure reactors for the same throughput. On the other hand, the amount of recycle gas can be kept lower, which allows reductions in other equipment, such as gas recirculation pumps, and piping dimensions.

Some pros and cons of the suspension versus the fixed bed hydrogenation process are as follows. The capital investment required for the suspension process is estimated to be somewhat lower than that for the fixed bed process. Costs of additional equipment for the separation of the suspended catalyst, the distillation of the crude fatty alcohol, and rework of the unreacted methyl ester is more than compensated by larger reaction vessels, gas recirculation pumps, and pipe work in the high pressure part of the fixed bed plant.

As far as the consumption of raw material is concerned, the fixed bed process has an advantage because the conversion of the ester into fatty alcohol is almost quantitative

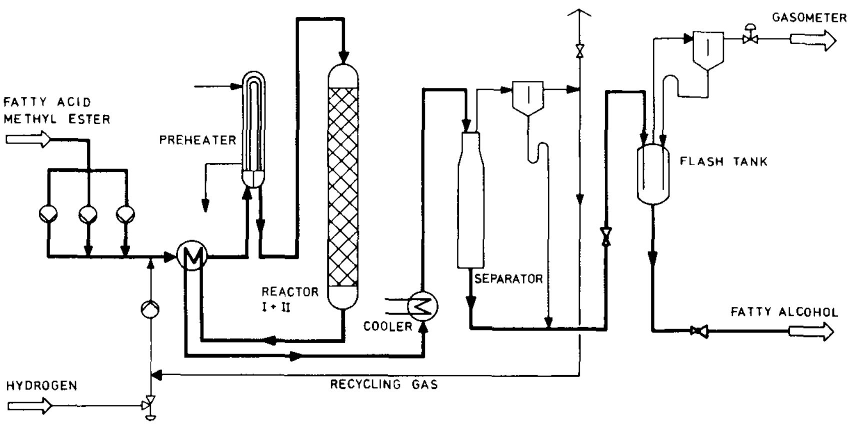

FIG. 5. High-pressure hydrogenation of fatty acid methyl esters – fixed bed process.

with a very low formation of hydrocarbons. The catalyst consumption of the suspension process, which is in the range of 0.4-0.7%, is considerably higher than in the fixed bed process (0.2-0.3%). Energy consumption is estimated to be in the same order of magnitude, the suspension process requiring higher temperatures, and the fixed bed process having a larger power installed for bigger recirculation pumps and compressors.

The quality of the crude fatty alcohols resulting from the fixed bed process is better, with a lower hydrocarbon content and lower saponification values. The fatty alcohol of the suspension process can be brought up to the same quality level; however, this requires an additional purification step.

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West European Household Detergent Trends

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ABSTRACT

It is estimated that there will continue to be a relatively strong growth in demand for alcohol derivatives, ca. 3 times as high as that for the product sector as a whole. Detergent alkylate growth will be somewhat lower, but it will remain the staple diet of the industry and by far the single largest volume detergent intermediate.

Household detergents – both the heavy-duty products used for the domestic laundry and the light-duty washing-up liquids – constitute the single largest segment of various detergent market sectors. In terms of active matter, it represents some 60% of a total annual West European demand currently running at ca. 1,200,000 metric tons.

The household market is tending towards maturity and its growth has now declined to levels below expected average West European GNP growth rates. Although the future detergent product growth rates may be modest in comparison with those of the 1950s and 1960s, the growth in demand for particular types of active matter is expected to be considerably higher. Within an overall modest growth rate for the product as sold to the consumer and assuming no change in average active matter content, a high relative growth rate for particular types of active matter can be achieved if products are reformulated.

The driving forces for the expected reformulation – particularly of the heavy-duty products – are provided by both environmental requirements and the need to maintain the products as new and innovative in the consumer's mind. Thus, even in depressed economic conditions, one would expect change to occur, and, particularly if this is coupled with improved cost performance of the product, change becomes inevitable.

It is necessary for a company like my own, a major supplier of detergent intermediates (the chemical derivatives of which find their way into the products sold to the consumer) to understand these formulatory trends if we are going to continue to be successful in providing products in the right volumes at the right times in response to market requirements.

LIGHT-DUTY LIQUIDS

Former growth rates of 7-8% per annum have declined and are expected to be of the order of 1-2% per annum until the end of the decade. The historical usage and expected future demand is shown in Table I.

The higher growth rate in the latter part of the decade is caused by some countries changing from powders to liquids.

Formulation of light-duty liquids has changed over the last 10 years principally as a result of the introduction of paraffin sulfonates. Further changes are expected as alpha olefin sulfonates (AOS) become increasingly available and afford the formulator the opportunity to improve the mildness of the product while maintaining detergency. The expected changes in demand for active matter are shown in Table I.

HEAVY-DUTY SECTOR

The heavy-duty product sector is by far the largest of the household product market, as shown in Table II. It is in this sector that environmental constraints have, and will continue for some time to have, a strong influence on the formulation of these products. Significant parameters in this context are:

- trend towards lower phosphate levels from 30-40% to ca. 20% backed by legislation in some countries;
- energy conservation lowering average wash temperatures from 60 C to 40 C;
- further slight increase of the synthetic component in the textile mix; and
- product cost/performance.

Although 2-3 years ago we expected the industry response to these requirements to be both higher active matter levels and increased usage of alcohol long-chain ethoxylates (nonionics), matters developed differently. Currently there are four separate trends or combinations of these: high nonionic based formulations, high bleach levels, use of bleach activators, and zeolite/phosphate combinations.

The basic expectation that usage of nonionics would increase was correct. It is relevant to point out that the reason for the use of long-chain ethoxylates was their lower sensitivity to hard water – compared to alkylbenzene sulfonate – and their efficiency in cleaning, particularly of synthetics. The use of these products also permitted the cost/performance of the product to the enhanced: washing efficiency was improved and the expensive phosphate component reduced. Additionally, heavy-duty liquids were introduced into Germany and France – two of the major detergent markets in West Europe – the majority of these liquids contain no phosphate; to compensate for this, they contain nearly 3 times as much active matter as powders per unit weight of product.

Although we expect that, for the reasons already cited, long-chain ethoxylates will continue to increase it is also