Production of Fatty Alcohols from Fatty Acids

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ABSTRACT

Detergent-range alcohols from natural feedstock can be produced by high pressure hydrogenation of either methyl esters or fatty acids. The increasing quantities of fats and oils on the world market secure a reliable and economically priced material. Although fatty acid is an abundant worldwide commodity, most alcohol producers hydrogenate methyl esters, because direct hydrogenation of fatty acids is difficult as the catalyst is sensitive to acid attack. The process described here makes it possible to hydrogenate fatty acids directly to alcohols of high quality without prior esterification. The reaction takes place in the liquid phase over a fine-grained copper chromite slurry in a single reactor vessel. A special reactor design with an optimum arrangement of the feeding nozzles causing an appropriate circulation of the reacting components inside the reactor facilitates the rapid "in situ" esterification reaction. This minimizes the free fatty acid concentration in the reactor to nearly zero. This results in a low consumption of catalyst. The most important advantages of the process are: direct feed of fatty acids of various origins, use of reasonably priced raw materials such as soapstock fatty acids and lower grade tallow acids, no process steps with methanol, and excellent economics. The process is industrially proven.

INTRODUCTION

The oil shocks drastically changed the prospects for natural oils and fats as raw materials for chemicals and intermediates.

Price indices of crude oil and naphtha, tallow and coconut oil between 1970 and 1981 in Deutschmarks (1) demonstrate the dramatic change in relationships. Starting from an index of 100, crude oil and naphtha increased nearly 10 times, whereas natural oil and fat remained fairly constant.

Ethylene, which became cheaper and cheaper during the 1960s and reached its minimum in 1970-73, rose in price and in 1981 exceeded even the price of, e.g., coconut oil. The maximum difference in favor of natural oil was reached in 1981/82. Since then, the development has to a certain extent been reversed. Figure 1 shows the development of the actual prices in ¢/lb (2).

The world production of natural oils and fats increased from 1974/75 to 1979/80 by ca. 25%, but ca. 90% of the increase was in vegetable oils and 10% in animal fats (3). Total fat production in 1979/80 was ca. 60 millions tons.

Fluctuations in availability and price have stopped the growth of detergent fatty alcohols made from petroleum-based raw materials. Recently installed new production facilities started again from natural feedstock.

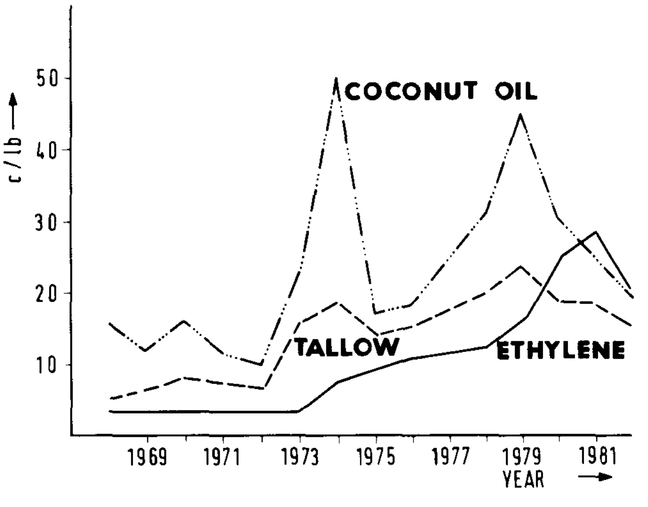

FIG. 1. Annual average prices for ethylene, tallow and coconut oil (2).

TECHNOLOGY OF FATTY ALCOHOL MANUFACTURING

For more than 50 years, natural fatty alcohols have been produced on an industrial scale by high pressure hydrogenation with catalytically activated hydrogen (4).

Meanwhile, three routes are technically proven, all of which operate at temperatures of 250-300 C and pressures of 200-300 bars: (a) hydrogenation over a fixed bed catalyst in the gas phase, (b) hydrogenation over a fixed bed catalyst in the trickle phase, and (c) hydrogenation in the liquid phase with suspended catalyst. All these processes yield fatty alcohols of excellent quality. Typical characteristics are the hydrogen recirculation ratio and the liquid hourly space velocity (LHSV) which are shown in Table I (5).

Hydrogenation Catalysts

Reduction of the carboxyl group by hydrogen is always accompanied by the generation of hydrocarbons of the same chain length, because this overhydrogenation is thermodynamically favored.

Fatty alcohols can only be produced with a highly selective catalyst. Hitherto, only copper-containing catalysts of different composition have been industrially successful for this purpose. However, these catalysts are very sensitive to typical catalyst poisons like S, Cl and P. Similar copper-containing catalysts have prevailed in other industrial processes, e.g., methanol Synthesis and low-temperature shift conversion, but they could not succeed until it became possible to desulfurize the raw material down to fractions of one ppm. In the low pressure methanol synthesis, for instance, the synthesis gas has to be desulfurized to 0.1 ppm to reach a catalyst consumption of less than 0.1 kg/ton MeOH and a minimum lifetime of the catalyst charge of 2 years.

These low sulfur contents are, however, not attainable in the hydrogenation of fatty acid esters or fatty acids. The sulfur contents of natural feedstocks are much higher and varying. In addition, they contain changing amounts of Cl and P stemming from pesticides and from previous processing steps.

There is no commonly acknowledged opinion about the toxicity of chlorine to copper catalysts; the very strong toxic effect is, however, undisputed. Most probably, chlorine leads not so much to clogging of the active centers but rather promotes the very undesirable recrystallization of the metallic copper.

Feedstock which contains varying amounts of catalyst poisons can be hydrogenated to advantage in the liquid phase with suspended catalyst, because it is possible to maintain the required catalytic activity by feeding an adequate amount of fresh catalyst to the reactor and purging the equivalent amount of spent catalyst. Production can remain fully onstream without interruption while the

TABLE I

Typical Process Characteristics of the Methyl Ester Hydrogenation

	Gas phase	Trickle phase	Slurry phase
H_2 /Ester ratio (mol/mol)	600	100	50
LHSV (v/v•hr)	1	0.4	1

whole catalyst charge is being replaced. The price to be paid for this flexibility and independence is, however, that a catalyst recovery section of the plant is required.

The specific catalyst consumption depends mostly on the S and Cl content of the feedstock. Technical experience shows, for instance, that 1 ppm sulfur above a certain level requires 1 kg additional catalyst per ton of fatty alcohol. Having adsorbed the sulfur, the catalyst is loaded with 1,000 ppm S and becomes nearly inactive. We cannot yet offer similar proven figures for chlorine.

Other damaging effects of the catalyst by thermal recrystallization, coking or reaction water are of minor importance. Blocking of the active surface by highly polar components like glycerol and monoglycerides should be avoided as it causes a higher catalyst consumption.

The copper-containing catalyst is, however, sensitive to acids and not without fail qualified for the hydrogenation of fatty acids. Therefore, effective measures have to be taken to eliminate the damage to the catalyst by acids. Traditionally this is performed with outstanding success by esterification of the fatty acid usually with methanol. This, however, has not only advantages but also involves the handicap of a certain methanol decomposition and of an additional methanol separation step being required.

Principle of the Lurgi Fatty Acid Hydrogenation Process (6)

Lurgi has developed a process which makes it possible to hydrogenate fatty acids directly, without previous esterification to fatty alcohols. Double bonds which may exist in the fatty acid chain are hydrogenated simultaneously.

The hydrogenation of fatty acids to alcohols takes place in the liquid phase at ca. 300 bar and 280 C. The overall reaction occurs in two stages over a fine-grained, slurried copper chromite catalyst, offered commercially by several companies. The first stage in esterification of the fatty acid with fatty alcohol to yield the ester plus water. The second stage in hydrogenation of the ester to two moles of alcohol. Both reactions occur simultaneously in a single reactor vessel of special design (7).

The reactor is a loop vessel with maximum internal recirculation facilitated by a very effective bubble separating system in the top of the reactor and an optimum arrangement of hydrogen jets and feeding nozzles for fatty acid and catalyst slurry in the bottom. The ratio of recirculated fatty alcohol to the fatty acid feed is more than 250, and effective dilution within a small volume provides optimum conditions for a rapid and complete esterification at reaction conditions.

The copper chromite catalyzes the above esterification reaction more rapidly than the hydrogenation. This results in a low catalyst consumption due to acid attack.

The second stage of the reaction proceeds slowly and requires a longer liquid residence time in the reaction vessel to obtain a good alcohol yield. Hydrogen is dissolved in the liquid phase under high pressure and diffuses to the catalyst surface where the hydrogenation reaction occurs.

In addition to these reactions, the unsaturated carbon chains are saturated with hydrogen. The saturation and hydrogenation reactions are both exothermic. The heat of hydrogenation is approximately constant for different acid feedstocks but the heat of saturation varies greatly, depending on the degree of unsaturation in the feedstock.

Description of the Process Plant

The process (Fig. 2) consists of a high-pressure section in which hydrogenation takes place, and a low-pressure section in which the alcohol is separated from the catalyst. The fatty acid reacts with hydrogen in the presence of slurried catalyst. The mixture of hydrogen, fatty alcohol and catalyst leaves the reactor at ca. 300 bar and ca. 280 C. The product mixture exchanges its heat with the circulating hydrogen.

Liquid alcohols and catalyst, hydrogen, low boiling fatty alcohols and reaction water are separated in a two-stage cooling/expansion system. The released hydrogen is returned to the make-up hydrogen.

The fatty alcohol/catalyst mixture passes from the feed tank to a centrifugal separator where the mixture is separated into a fatty alcohol/catalyst slurry phase and a

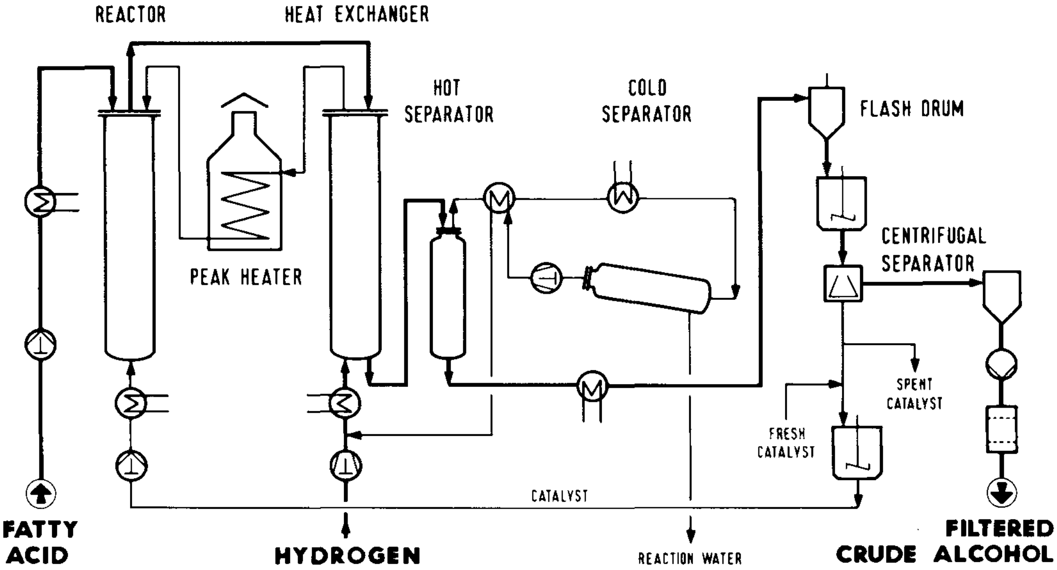

FIG. 2. Simplified process flow diagram for fatty alcohol synthesis via hydrogenation of fatty acids.

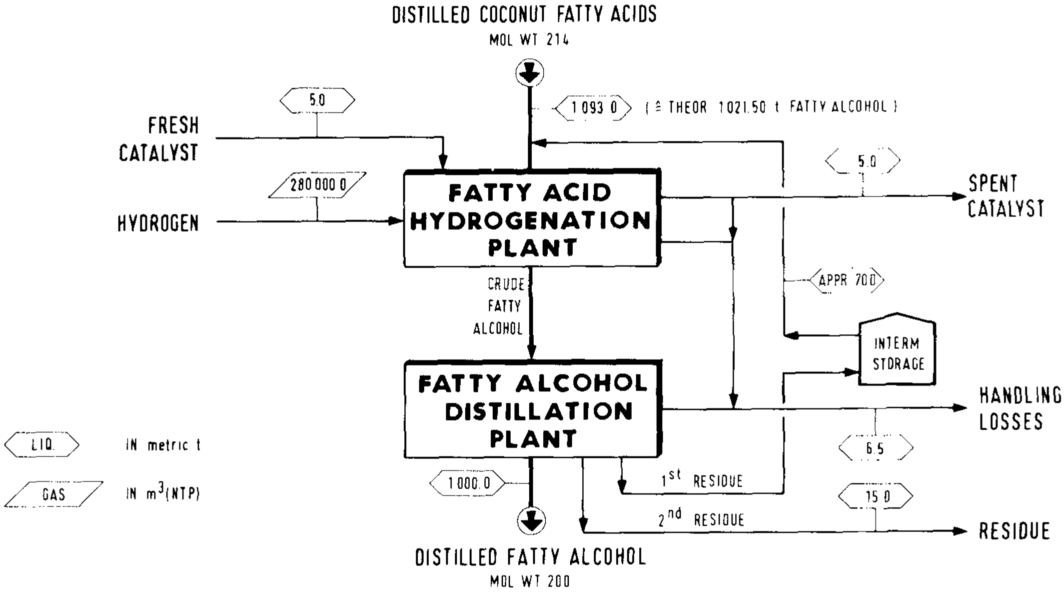

FIG. 3. Typical material balance for 1,000 tons fatty alcohol product feedstock: 100% coconut fatty acid.

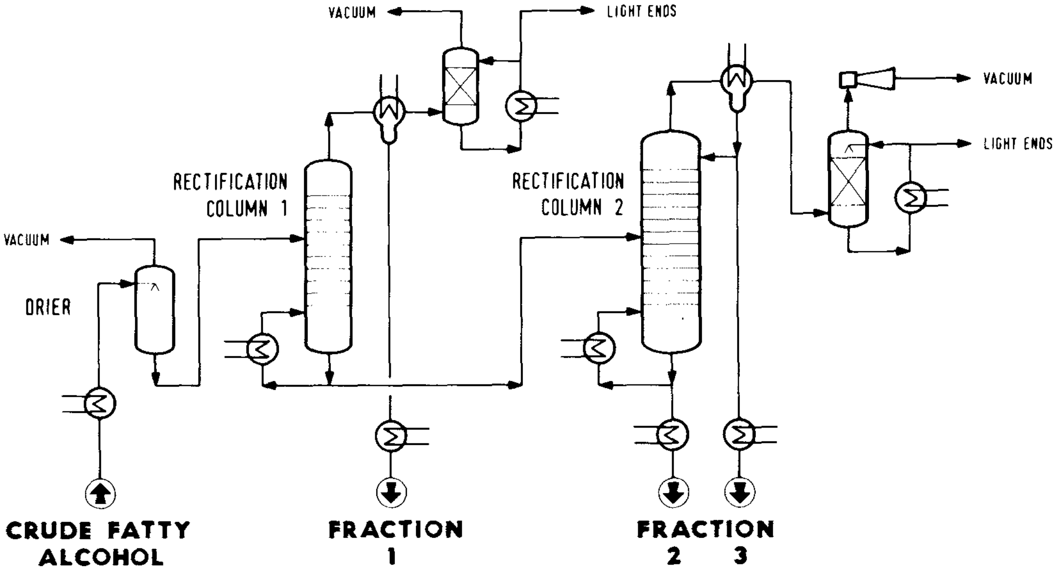

FIG. 4. Typical process flow diagram for fractionation of fatty alcohols.

clear phase. A polishing filter removes the last traces of solids and the clean crude fatty alcohol is pumped to the distillation unit or product storage.

A partial stream of the spent catalyst is bled continuously from the process and an equivalent quantity of fresh catalyst is added to the fatty alcohol/catalyst slurry mixture which then is pumped back to the reactor.

Material and Energy Consumption

Figure 3 shows an example of a specific overall material balance for 1,000 ton of distilled fatty alcohols produced, starting from distilled coconut fatty acids. Utilities consumed per ton of crude fatty alcohol produced are approximately as shown in Table II.

The crude fatty alcohol has an acid number below 0.1 mg KOH/g; saponification value of 2-5 mg KOH/g and less than 1 wt % of hydrocarbons.

Distillation and Fractionation of Fatty Alcohols

A typical fractionation unit for coconut fatty alcohols is shown in Figure 4.

TABLE II

Utilities Per Ton of Crude Fatty Alcohol Produced

Catalyst	5 kg
Electric power	130 kWhr
Steam (15 bar)	170 kg
Energy for peak heating	1.15×10^6 kj
Cooling water (Δ T 10 C)	20 m^3

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