

Catalyst in Basic Oleochemicals

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Abstract

Currently Indonesia is the world largest palm oil producer with production volume reaching 16 million tones per annum. The high crude oil and ethylene prices in the last 3 – 4 years contribute to the healthy demand growth for basic oleochemicals: fatty acids and fatty alcohols. Oleochemicals are starting to replace crude oil derived products in various applications. As widely practiced in petrochemical industry, catalyst plays a very important role in the production of basic oleochemicals. Catalytic reactions are abound in the production of oleochemicals: Nickel based catalysts are used in the hydrogenation of unsaturated fatty acids; sodium methylate catalyst in the transesterification of triglycerides; sulfonic based polystyrene resin catalyst in esterification of fatty acids; and copper chromite/copper zinc catalyst in the high pressure hydrogenation of methyl esters or fatty acids to produce fatty alcohols. To maintain long catalyst life, it is crucial to ensure the absence of catalyst poisons and inhibitors in the feed. The preparation methods of nickel and copper chromite catalysts are as follows: precipitation, filtration, drying, and calcinations. Sodium methylate is derived from direct reaction of sodium metal and methanol under inert gas. The sulfonic based polystyrene resin is derived from sulfonation of polystyrene crosslinked with di-vinyl-benzene. © 2007 CREC UNDIP. All rights reserved.

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1. Introduction

Palm plantation shows high growth in the last 10 years. Indonesia has surpassed Malaysia in palm oil production for the first time in year 2006. Both countries produce more than 80% of total world production. Table 1 shows palm oil production from 2002 to 2006. With the ever-increasing palm plantation acreage, the Indonesian palm oil production will continue to increase much faster than Malaysian. On the other hand, the high crude oil and ethylene prices in the last 3-4 years contribute to the healthy demand growth for basic oleochemicals: fatty acids and fatty alcohols .

Oleochemicals are starting to replace crude oil derived products in various applications. Stearic acid is replacing paraffin wax in candle making, meanwhile natural fatty alcohol replacing synthetics. The relentless climb of palm oil production and the recent high crude oil price encourage significant growth of Indonesian basic oleochemicals.

In the early 20th century, the commercial production of fatty alcohol was derived from direct sodium hydrogenation of sperm oil from whales (1). Later, many countries listed sperm whales as endangered species and banned the importation of their product derivatives. The fatty alcohol produc-

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Table 1. Palm Oil Production (in thousand tones)

| | 2002 | 2003 | 2004 | 2005 | 2006 |
|-----------|--------|--------|--------|--------|--------|
| Malaysia | 11,908 | 13,354 | 13,974 | 14,961 | 15,880 |
| Indonesia | 9,370 | 10,600 | 12,380 | 14,000 | 15,900 |
| Others | 3,756 | 3,926 | 3,586 | 4,769 | 5,000 |
| Total | 25,034 | 27,880 | 29,940 | 33,730 | 36,780 |

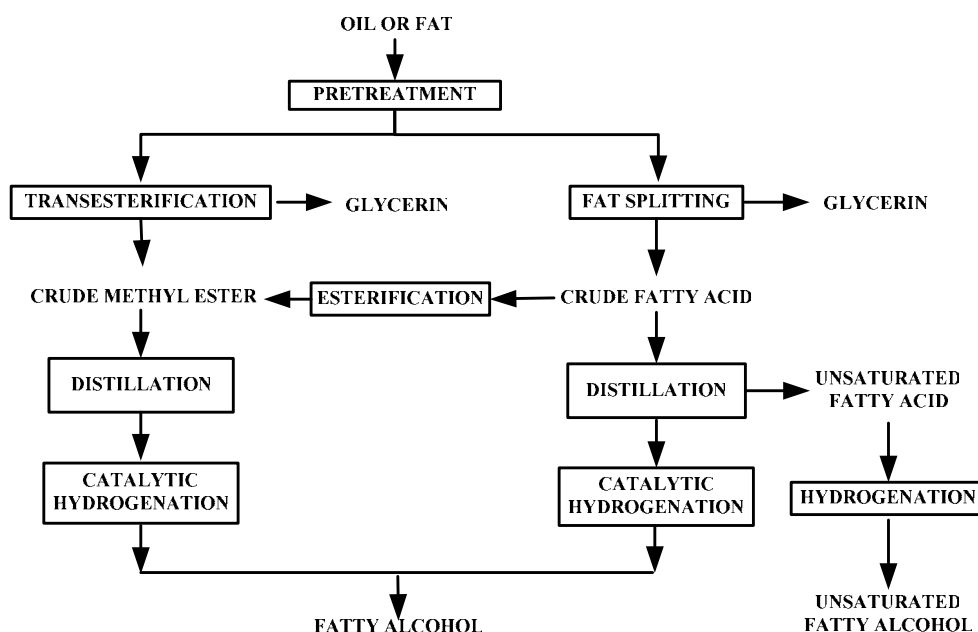


Figure 1. The effect of reaction time on the polymerization of acrylonitrile: Reaction condition: 0.5 g exchanged bentonite; acrylonitrile 1.886 mol.dm⁻³; K₂S₂O₈ 0.03 mol.dm⁻³ at different temperature

ers then switched their starting raw materials to tallow, lard, coconut oil, palm kernel oil, and castor oil. Since the mid 1950s, catalytic hydrogenation to produce fatty alcohol from natural fats and oils was proved to be more economical and replaced metallic sodium hydrogenation.

It is plausible to produce fatty alcohol from direct catalytic hydrogenation of triglycerides. However, the catalyst and hydrogen consumptions are higher because by-product glycerin will be simultaneously hydrogenated to produce propylene glycols and propanol. Moreover, glycerin and glycerides were found to be poisonous to the hydrogenation catalyst. The current practice of fatty alcohol production begins with separating the glycerin from fatty acid/methyl ester before hydrogenate the fatty acid/methyl ester further to fatty alcohol. The modern manufacturing routes of basic oleochemicals are shown in Figure 1.

As widely practiced in petrochemical industry, catalysts also play a very important role in the production of basic oleochemicals. The invention and development of highly selective catalysts often improve the economic competitiveness of basic

oleochemicals and thus enhance their widespread use. This paper is intended to review the catalytic process in the production of basic oleochemicals.

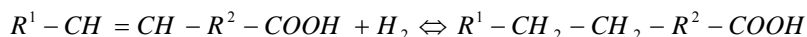
2. Catalytic Process in Basic Oleochemicals

2.1. Unsaturated fatty acid hydrogenation

Saturated fatty acids, naturally exist as straight chains, do not contain any double bonds or other functional groups along the chain. Whereas unsaturated fatty acids are of similar form, except that one or more alkene functional groups exist along the chain, i.e.: each alkene substituting a single bond "-CH₂-CH₂-" part of the chain with a double bond "-CH=CH-". Unsaturated fatty acids are naturally found in vegetable oils, including palm oil, palm kernel oil, and soybean oil.

Unsaturated fatty acids are often not desirable in a number of fatty acid industrial applications, such as: metal stearates, rubber compounding, candles, waxes, and crayons. The presence of double bond lowers the melting point and reduces the shelf-life and heat stability due to vulnerability of the double bond toward ambient oxidation.

To improve the shelf-life and increase the melting point, the unsaturated fatty acids are converted to saturated fatty acids by the relatively simple hydrogenation reaction:



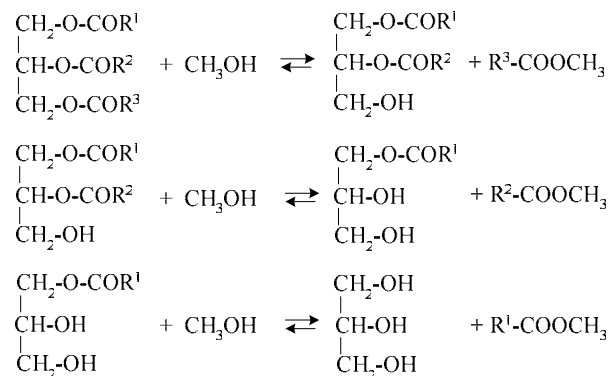
A great care on the choice of catalyst, reaction temperature, and reaction pressure should be taken to avoid hydrogen attacking the carboxyl group during the hydrogenation of double bond. The heterogeneous catalyst normally used in the hydrogenation of unsaturated fatty acids is nickel based catalyst.

Figure 2 shows process flow diagram of industrial scale unsaturated fatty acid hydrogenation. The unsaturated fatty acid is first passed through a dryer, mixed with hydrogen, added with nickel catalyst slurry, and hydrogenated at 25 atm and 453–523 K in a buss loop or slurry reactor. The sulfur, phosphorus, bromine and nitrogen compound in the feed should be minimized to below 1 ppm, because they are poisons to the nickel catalyst. By product nickel soaps are produced as side reaction from this process.

The nickel catalyst is prepared by precipitating a nickel salt, usually sulfate or chloride, on an inert support, such as silica, alumina, or a combination thereof. The precipitate is filtered, washed, and dried. The resulting powder is then reduced with hydrogen at 753 – 813 K, coated with triglyceride fat, chilled, and formed into pellets (2).

2.2. Methyl ester by transesterification

The reaction mechanism of transesterification can be described as follows:



In the reaction, a large and branched triglyceride (TG) is reacted with methanol to produce diglyceride (DG) and methyl ester. DG is then reacted further with methanol to produce monoglyceride (MG) and methyl ester. Finally MG reacts with methanol to produce glycerol and methyl ester. All the three reaction steps are reversible and at the end of the transesterification reaction usually a small percentage of MG remain in the product mixture.

A process flow diagram of continuous methyl ester production by transesterification is shown in Figure 3. Natural oils or fats are mixed with excess methanol and homogeneous alkali-based

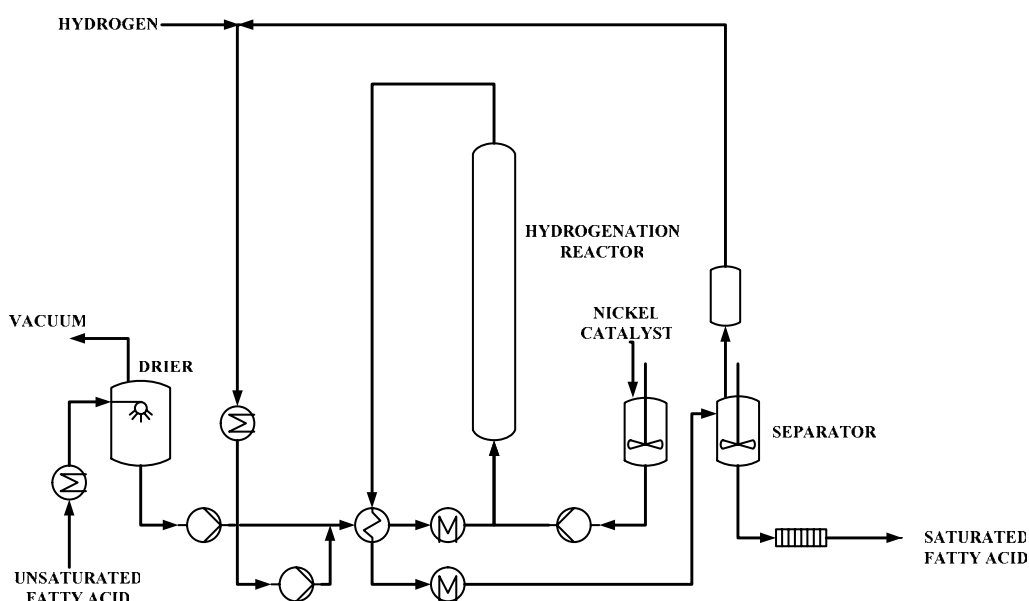


Figure 2. Unsaturated Fatty Acid Hydrogenation

catalyst at atmospheric pressure and 333 – 338 K in a continuous stirred tank reactor. Common catalyst for transesterification is alkali-based (3), due to its higher reactivity than the acid. The acid-catalyzed transesterification is normally three orders of magnitude slower than the alkali. Moreover, acid-based catalyst is highly corrosive.

The residence time of reaction mixture in the stirred reactor with homogeneous alkali-based catalyst is about 1-2 hours. In order to achieve a complete transesterification, it is often desirable to have a transesterification plant with two continuous stirred reactors in series.

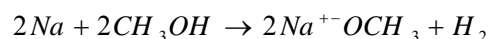
The use of homogeneous alkali-based catalysts limits the choice of feedstock to refined oil with very low free fatty acid (FFA) because FFA consumes the alkali based catalyst to produce soap in the glycerin-water. The presence of soap also increases the glycerin-water viscosity, increases the concentration of monoglyceride in the glycerin-water, and complicates the separation of fatty matters from glycerin.

It is also crucial to maintain a very low level of water in the reaction mixture of transesterification. The presence of water will consume alkali-based catalyst, forms hydroxide ion which then reacts with oil to form soap, and hamper the completeness of transesterification reaction. Ma, et al. (4) reported that water and FFA content should be maintained below 0.06 wt% and 0.5 wt% respectively in order to have a complete transesterification of beef tallow under alkaline condition. The low water content is more crucial than the low FFA content.

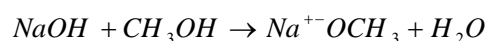
Sodium methoxide, caustic soda, potassium hydroxide, and sodium octoxide are examples of

homogeneous alkali-based catalyst. Metal alkoxide, such as sodium methoxide, is the most effective catalyst for transesterification due to its high alkalinity. Methoxide ion easily attacks triglycerides and releases them as methyl ester.

Sodium methoxide is commercially produced from reaction of sodium metal and methanol under inert gas:



Caustic soda and potassium hydroxide can also provide methoxide ion in methanol solution. However, water is generated:



The presence of water interfere transesterification (4).

Figure 4 shows the typical performance of four different alkaline catalysts in methanol solution in laboratory scale transesterification. The percentage of MG remained in methyl ester indicates the performance of each catalyst to complete the transesterification reaction. Sodium methoxide is the best catalyst with methyl ester yield of up to 99% and has the least MG in the methyl ester.

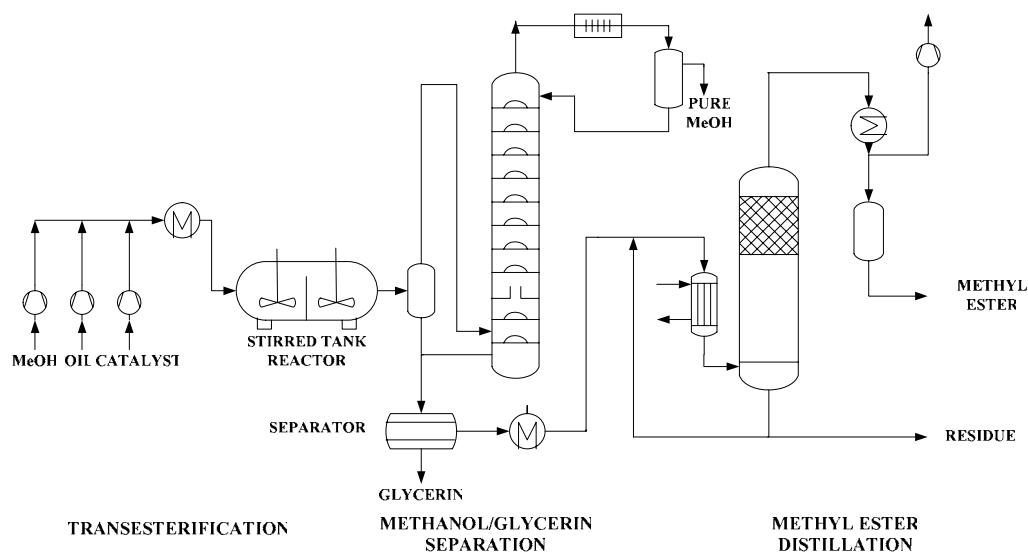


Figure 3. Methyl Ester by Transesterification

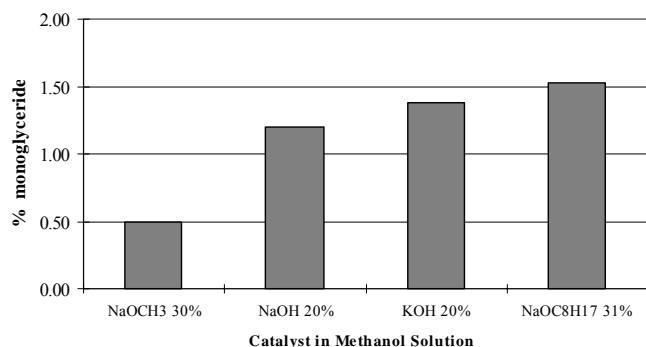
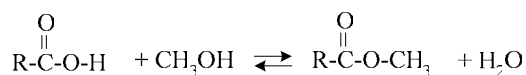


Figure 4. % Monoglyceride in Methyl Ester with Different Catalysts

2.3. Methyl ester by fatty acid esterification

The reaction to produce methyl ester from fatty acid esterification is as follows:



Fatty acid is simply reacted with methanol to produce methyl ester and water. The reaction is reversible and the presence of water will inhibit the esterification reaction. To have a complete conversion of fatty acid to methyl ester, water should be continuously withdrawn from the reaction mixture.

Fatty acid esterification can be catalyzed by homogeneous or heterogeneous acid catalyst. Soluble acid catalyst normally used is sulfonic acid or any other strong acid, such as: sulfuric acid and hydrochloric acid. Para-toluene sulfonic acid is the preferable homogeneous catalyst due to less corrosive compared to the inorganic acids.

The use of homogeneous catalyst creates problem in the separation and the recovery of the catalyst from methyl ester. To overcome the problem, several types of solid catalysts for fatty acid esterification have been developed. One of the preferred solid acid catalysts used is a polystyrene resin. The polystyrene is cross-linked with di-vinyl-benzene to form macroporous strong acidic polystyrene resin catalyst. Esterification using resin catalyst is temperature-limited; higher temperature will cause the catalyst degraded excessively. However, a single stage laboratory batch esterification process, catalyzed by resin at 373 – 403 K, is able to give more than 95% in conversion, as shown in Table 2.

Fatty acid esterification by methanol can be carried out either in a batch reactor or in a continuous counter current reactive distillation column filled with resin catalyst (5,6). In the industrial batch process, fatty acid is reacted with

methanol under atmospheric pressure at temperature as low as below 343 K, limited by the methanol boiling point. While in a continuous reactive distillation column, the reaction can be carried out at higher temperature, up to 403 K. The withdrawal of water to ensure the complete conversion of fatty acid to methyl ester in a batch reactor is a challenge because methanol as one of the reactant has a lower boiling point than water.

Table 2. Fatty Acid Esterification Using Various

| | -1 | -2 | -3 | -4 |
|-----------------------------|-----|-----|-----|-----|
| Max. operating temp (K) | 63 | 13 | 03 | 03 |
| Conversion (%) at 373-403 K | 6.3 | 6.4 | 7.1 | 6.4 |

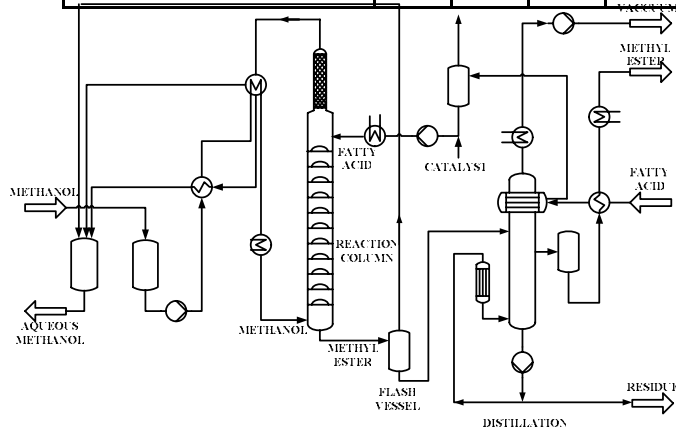


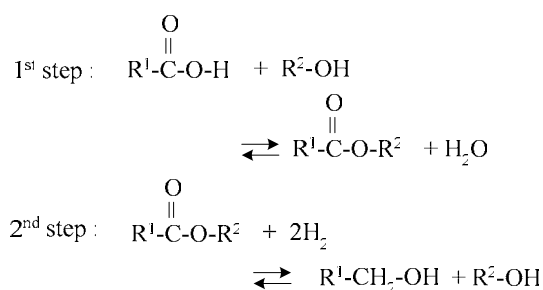
Figure 5. Methyl Ester by Fatty Acid Esterification

Figure 5 shows process flow diagram of a continuous esterification process in a reactive distillation column filled with resin catalyst. At the top of the esterification column, fatty acid is introduced while water and excess methanol are continuously withdrawn. The iron content in the fatty acid feed should be maintained below 1 ppm because iron is poisonous to the resin catalyst. At the bottom of the column, fresh methanol is introduced and methyl ester is counter current continuously withdrawn. To ensure complete conversion of fatty acid to methyl ester, it is important to minimize water in the column and inject fresh methanol into bottom of the reactor. It is imperative to have methyl ester with low fatty acid in fatty alcohol synthesis because fatty acid is poisonous to high pressure hydrogenation catalyst. A small amount of dimethyl ether, as an etherification result of 2 methanol molecules, appears as side reaction product of fatty acid esterification.

2.4. Slurry process of high pressure fatty acid hydrogenation

In 1931, Adkins, Norman, Schmidt and Schrauth simultaneously reported that copper chromite (CuCr) catalyst can selectively hydrogenate carboxylic compound into their corresponding fatty alcohol (7,8,9,10). Fatty acid can be directly hydrogenated with a CuCr catalyst at temperature up to 573 K and 200-300 atm to produce fatty alcohol. However, the CuCr catalyst is prone to attack by fatty acid to produce copper soap so that the catalyst consumption will be high (11).

To circumvent the fatty acid attack on the CuCr catalyst, Lurgi (12) has developed a suspension process that re-circulates CuCr powder catalyst slurry covered in fatty alcohol into the high pressure hydrogenation reactor at 553 K and 300 atm. The re-circulated fatty alcohol covering the CuCr catalyst powder first reacts with fatty acid to produce wax ester in the first step. Afterward, the CuCr powder catalytically converts the wax ester into fatty alcohol in the second step. The reaction mechanism is as follows:



Essentially, the process is not a direct hydrogenation of a fatty acid. It is the hydrogenation of wax ester formed in the first reaction step.

The slurry process flow diagram of the high pressure fatty acid hydrogenation plant developed by Lurgi (12) is shown in Figure 6. The process involved handling the circulation of fatty alcohol/catalyst slurry phase. The CuCr catalyst consumption is rather high up to 5 kg/ton of fatty alcohol produced partly because reaction of fatty acid with copper in the catalyst. Aldehyde, alkane, wax ester, di-alkyl ether, and copper soap are undesirably produced as side reaction products from this process. Copper soap tends to precipitate as deposit in downstream piping and process equipments. The hydrocarbon and the unreacted wax ester content in the reactor outlet are relatively high at 1 wt% and 3 wt% respectively.

The CuCr powder catalyst is prone to poisons, such as:

- Sulfur form Cu-Sulfide which causes permanent catalyst deactivation (limit: 5 ppm S)
- Chloride adsorption triggers sharp permanent catalyst deactivation (limit: 2 ppm Cl)
- Phosphor adsorption causes soft catalyst deactivation (limit: 1 ppm P)
- Highly polar components, such as: glycerol, fatty acids, and monoglyceride, inhibit the activity by blocking active site on catalyst surface.

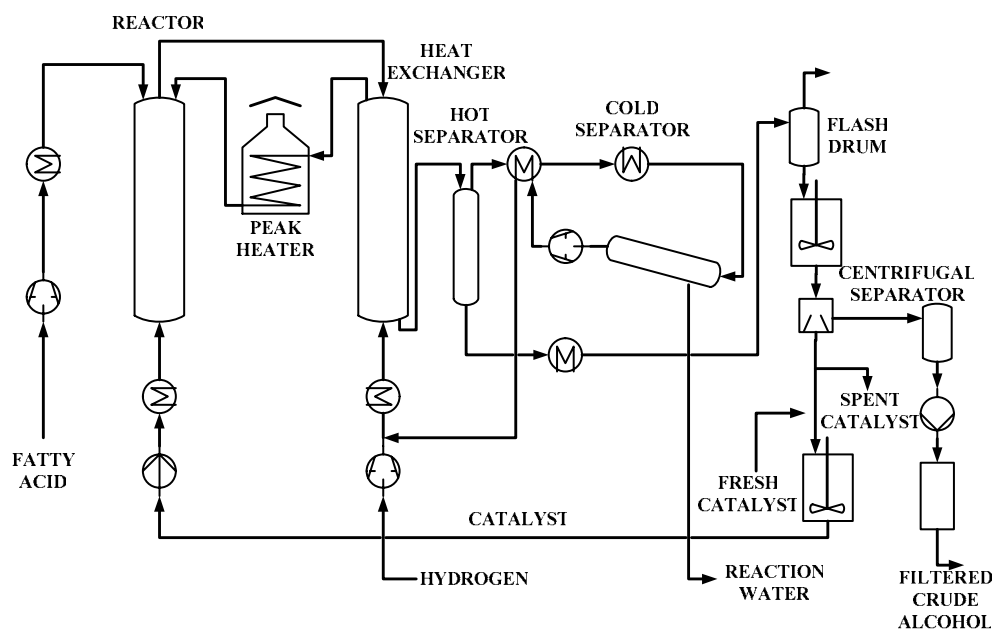


Figure 6. Lurgi Slurry Process High Pressure Fatty Acid Hydrogenation (12)

2.6 Fixed-bed process methyl ester high pressure hydrogenation

High pressure hydrogenation of methyl ester to fatty alcohol is usually preferable because CuCr catalyst is not sufficiently resistant to fatty acid. The hydrogenation of methyl ester is described in the following chemical reaction:



Since the methyl ester is relatively non-toxic or mild to the CuCr catalyst, the fatty alcohol production by high pressure hydrogenation of methyl ester can be carried out in a fixed-bed reactor (13). There are several types of pelletized catalyst that can be used in high pressure hydrogenation:

- CuCr gives the best performance for saturated fatty alcohol with typical composition: 37% Cu, 32% Cr, 3% Mn
- Copper zinc, example: 14%Cu/9%ZnO/SiO₂ (chrome free catalyst)
- Zinc chromite, has high selectivity to produce unsaturated fatty alcohol without attacking double bond in the methyl ester

Figure 7 shows process flow diagram of fixed-bed hydrogenation at 200-300 atm and 453-573 K. The methyl ester liquid is pumped, mixed with pressurized hydrogen, and heated up by heat interchange with reaction mixtures leaving the reactor before entering the fixed-bed reactor filled with CuCr catalyst. Inside the reactor, the liquid methyl ester trickles down over CuCr catalyst pellet, diffuses into the catalyst pores and converts to fatty alcohol on the catalyst active sites (see Figure 8). Similarly the hydrogen at

high pressure dissolves into the liquid trickle phase, diffuses into the catalyst pores, and arrives at catalyst active sites. The residence time of the liquid phase in the fixed-bed reactor is 5 minutes. After leaving the reactor, the reaction product is cooled. Excess hydrogen is separated and recirculated back into the reactor. The catalyst consumption of fixed-bed methyl ester is below 2 kg/ton of fatty alcohol, which is much lower than the catalyst consumption in the slurry process.

Undesirable impurities can be formed from side reactions. Primary alcohols can dehydrogenate to aldehydes and increase the carbonyl value of products. Thermal process could dehydrate alcohols to hydrocarbon formation like alkanes and initiate wax ester formation. Trace amount of fatty acids in the feed can leach copper from catalyst and form copper soaps. The hydrocarbon and the un-reacted methyl ester content in the reactor outlet are typically at 0.5 wt% and below 1 wt% respectively. The quality of crude fatty alcohol produced from the fixed-bed process is much better than slurry process, with a lower hydrocarbon and lower un-reacted methyl ester content.

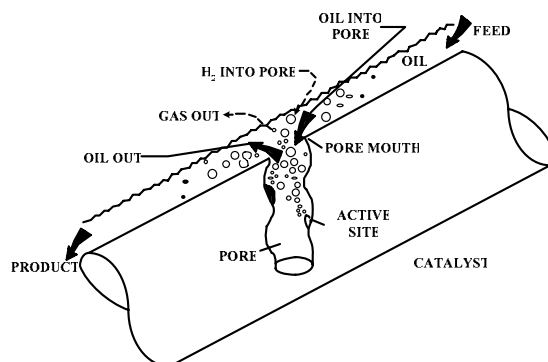


Figure 8. Trickle Bed Catalyst

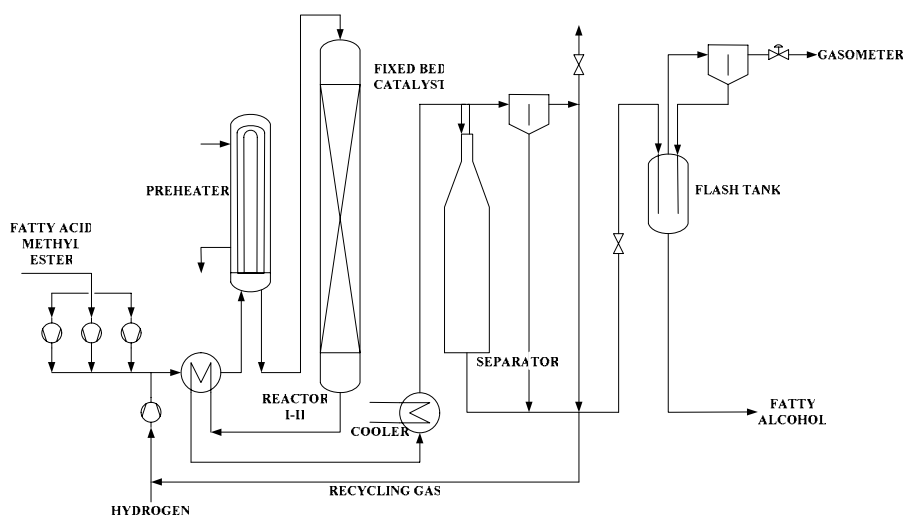


Figure 7. Methyl Ester High Pressure Hydrogenation Fixed-Bed Process

Similar poisons found in the slurry process, such as: sulfur, chloride, fatty acids, glycerol, and monoglyceride, can seriously damage and deactivate the CuCr catalyst pellet.

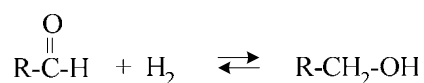
CuCr catalyst is manufactured using copper solution as nitrate and chromic acid at 303 K. $\text{CuNH}_4\text{OHCrO}_4$ will be precipitated under bubbling of anhydrous ammonia until pH 6.8 (14). The precipitated catalyst is then filtered, dried, and calcined at 723 K. After calcinations, it is ready to be used as powder catalyst. To obtain the catalyst in pellet form, the powder is extruded. Hydrogenation is necessary to attain reduced CuCr catalyst.

2.6 Fatty alcohol polishing

Fatty alcohol polishing is required to remove carbonyl-group compound existed in fatty alcohol products. A polishing can also remove color-bodies which usually consist of various saturated and conjugated compounds. The color is removed by hydrogenation of those unsaturated. The removal of unsaturated helps to improve the storage stability of the product. The effect of the impurities is oxidation of the product and results more color or bad-smell. The bad-smell due to oxidation is derived from cyclic ketones.

Beside the carbonyl value of fatty alcohol, the effect of polishing is also reflected in heat stability test. Typically, a polishing is run at very moderate conditions, but uses a highly active catalyst. They should be an extremely low level of poisons like sulfur. Together with the moderate conditions this leads to a long catalyst life of up to 5 years.

The polishing process is occurred under 25 atm at below 403 K in a fixed-bed reactor, with the chemical reaction as follows:



Carbonyl value can be reduced from 200 to below 20 ppm as CO after polishing process. Nickel based catalyst characteristics used for fatty alcohol polishing:

- Typical composition : 52 % Ni, 33 % Al_2O_3 , 3 % SiO_2
- Surface area: 215 m^2/g

Microfilter is usually used to avoid traces of catalyst fines leaving the polishing reactor. Traces of Ni (ppb-levels) can promote the unwanted reactions during storage of the alcohol, especially in the presence of air.

Figure 9 shows process flow diagram of fatty alcohol polishing. The high carbonyl fatty alcohol is mixed with hydrogen and trickled down

through the nickel catalyst pellet in the fixed-bed reactor. The reactor outlet is then passed through a hydrogen knock-out drum separating the hydrogen from low carbonyl fatty alcohol. The separated hydrogen is recycled back into the reactor.

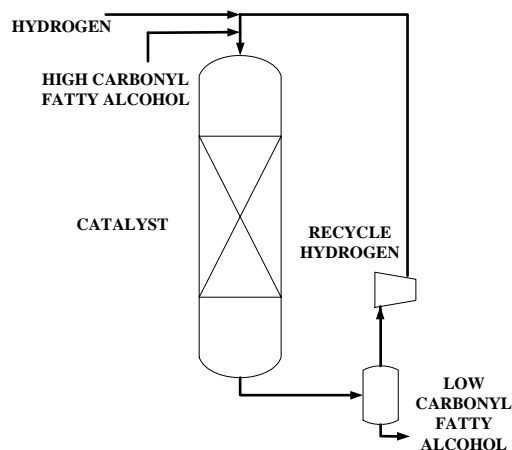


Figure 9. Fatty Alcohol Polishing

Nickel based catalyst is manufactured by heating elemental nickel to 1173 K. Molten aluminum is poured over the nickel shot, and then the molten alloy is poured into a mold for cooling and milled dry in a ball mill. The alloy is activated by exposure to sodium hydroxide solution at a pH of approximately 14. The temperature is maintained at 308 K or below and the pH is not allowed to go below 11.5.

3. Recent Technology in Basic Oleochemicals

3.1 Solid catalyst for vegetable oils transesterification

As mentioned in Section 2.2, there are three drawbacks of using homogeneous alkaline-based catalysts in transesterification experienced by current biodiesel operators. First, the catalyst is practically impossible to be separated and recovered. Second, the catalyst reacts with FFA and water, therefore it limits the choice of feedstock to refined oil with very low FFA and low water content. Third, the catalyst reacts with feedstock to produce soap in glycerin-water, complicates treatments for separation of fatty matters from glycerin, and generates salt during glycerin purification. The salt will eventually accumulate in the glycerin pitch and complicate the pitch disposal.

Several investigators have reported their endeavor to look for a suitable heterogeneous

catalyst for transesterification to produce methyl ester from oil feedstock with high FFA (15). Mixed metal oxide having the perovskite structure, such as calcium titanate, is one of the choices researched today (16). Phosphates of trivalent metals such as aluminium and ferric orthophosphates make suitable catalysts as well (17). 12-Tungstophosphoric acid (TPA) impregnated on hydrous zirconia, silica, alumina, or activated carbon was also evaluated (18). Some researchers focus in utilization of alkaline earth metal hydroxides, oxides, and alkoxides to catalyze the transesterification (19). Nevertheless, none of these heterogeneous catalysts give better performance than the homogeneous catalyst. Therefore, research in this area is still challenging.

3.2 Low pressure vapor phase hydrogenation

Davy Process Technology offers alternative route to produce fatty alcohol from natural oil and fats. The feed to hydrogenation should be in vapor phase. Davy route splits oil to fatty acid, transesterifies the fatty acid to methyl ester using methanol, and hydrogenates the methyl ester to fatty alcohol (20). Esterification of fatty acids uses resin as catalyst in reaction column as explained earlier. The new breakthrough is hydrogenation of methyl ester at low pressure using fixed-bed reactor with copper-zinc catalyst that is conducted at 483 – 508 K and 40 atm. The residence time of vapor phase methyl ester in the reactor is approximately 30 - 60 seconds. The core of this catalyst is copper which is active in reduced condition. Sulfur content in methyl ester is poisonous to the catalyst as well as fatty acid. The sulfur will deactivate catalyst to copper sulfide and the fatty acid will initiate copper soap.

3.3 Wax ester hydrogenation

Lurgi offers a new route to produce fatty alcohol from natural oil and fat, wax ester route. The wax ester route is carried out with fixed-bed hydrogenation and additional handling section as required in the earlier technology is unnecessary. It is conducted at 443 - 573 K and 200-300 atm. Firstly, natural oil is splitted to fatty acid and glycerin. Then the fatty acids are divided into cuts to be marketed and cuts for producing fatty alcohol. Only fatty acid desired as fatty alcohol is fed to wax ester process. Fatty acid is esterified with half of alcohol generated from hydrogenation to wax ester. Wax ester is charged to hydrogenation reactor, together with hydrogen. In a fixed-bed reactor, the ester liquid trickles downwards through the catalyst packing, forming

fatty alcohols in the process (21). The catalyst used is similar as previous Lurgi methyl ester hydrogenation process, CuCr. Half of fatty alcohols generated are recycled to esterification section. Free fatty acid will be poisonous to hydrogenation catalyst because it will form copper soap. The side products of this route are copper soaps, aldehydes, alkenes, and wax ester.

4. Conclusion

This paper has reviewed the contribution of catalyst and catalysis science to economically produce high quality basic oleochemicals. Actually catalyst science also flourishes in the production of other chemicals derived from basic oleochemicals, such as: propylene glycol from glycerin (22), fatty amines from fatty acid and/or fatty alcohol, ester quats from fatty acids and alkyl polyglycosides from fatty alcohol. Catalyst science plays an important role in the advancement of oleochemicals industry.

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