Journal of Oil Palm Research Vol. 23 December 2011 p. 1129-1134

NOVEL CATALYTIC SOLUTIONS FOR OLEOCHEMICAL PROCESSES

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ABSTRACT

Catalytic processes are key to meeting the growing demand for sustainable industrial chemicals derived from oils and fats, thus ensuring the sustainability and profitability of the oleochemical industry. This article focuses on novel catalytic solutions for both existing and new processes, giving focus to raw materials, energy and the environment. Practical examples will be given of lower-metal catalysts, processing of lower-grade feedstocks, and the treatment of fatty alcohols and methyl esters.

Keywords: nickel catalyst, hydrogenation, fatty acids, fatty alcohols, methyl esters.

Date received: 11 August 2010; **Sent for revision:** 28 October 2010; **Received in final form:** 10 February 2011; **Accepted:** 25 July 2011.

INTRODUCTION

The economic value of catalysis is enormous as more than 80% of all chemical products come into contact with a catalyst at some stage or other during their synthesis, thus rendering catalysts indispensable for the needs of the chemical industry today (Beller, 2007). For the oleochemical industry in particular, catalytic processes are key to supporting the growing demand for sustainable industrial chemicals derived from oils and fats.

Although catalyst costs are marginal compared to the total variable costs of production, there is a continued drive in search of catalysts with a longer life-span or a lower metal content (usually the most expensive ingredient). In this article, an illustrative example will be given for fatty acid hydrogenation using nickel slurry catalysts.

Catalyst lifetime can be significantly prolonged by extensive feedstock purification in order to remove all possible catalyst poisons. However, there is continuous pressure to decrease purification costs in order to decrease energy consumption and to enable the cost-effective treatment of recycle streams and lower-grade feedstocks. Oxidative stability and colour improvement by hydrogenation over current nickel catalysts is an example for which new nickel catalysts have become available. Although nickel is susceptible to many impurities, catalyst design has allowed for the cost-effective treatment of lower-grade feedstocks.

Due to their intrinsically sustainable character, catalysts (which are not used stoichiometrically in chemical transformations) should always be considered for chemical reactions. An example is the replacement of chemical reductants, such as sodium borohydride, for fatty alcohol polishing by catalytic hydrogenation over nickel catalysts.

Within polishing applications, a novel development is the hydrogenation of methyl esters to achieve very low iodine values. Fully hydrogenated FAMEs are excellent feedstocks for sulphonation to methyl ester sulphonates (MES) which display excellent detergent and environmental properties. This is a good example of a growing market that is based on sustainable and renewable feedstocks.

LOWER-NICKEL CATALYSTS

Supported nickel catalysts are widely used in the edible oil and oleochemical industries for the slurry-phase hydrogenation of triglycerides, fatty acids and their derivatives. The catalyst product is supplied in the form of pastilles, typically in the size range of 2-5 mm. These pastilles consist of catalyst

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particles dispersed in a saturated fat, protecting the reduced nickel catalyst from an oxidative environment. The catalyst particles themselves are typically in the micron range and consist of reduced metallic nickel dispersed in a support material, *e.g.* kieselguhr, silica or alumina. After dosing the reactor system, the catalyst pastilles are melted in a non-oxidising atmosphere (typically nitrogen, at 70°C-120°C), thereby freeing the active nickel catalyst for the hydrogenation reaction.

The nickel content in commercial catalysts is typically 22% nickel on a weight basis, and therefore it significantly contributes to the production costs. The nickel market is highly volatile and can be subject to large price fluctuations; for example, in May 2007 a peak price of USD 54 000 t^{-1} was reached.

Recent catalyst advances have resulted in the development of a lower-nickel catalyst for fatty acid hydrogenation. The PRICAT^{TM} 9953 has a nominal content of 19% nickel and is a direct replacement for existing 22% nickel fatty acid catalysts. Even with a lower amount of nickel in the catalyst, the same performance can be reached, as can be seen in *Figure 1a* for a palm oil fatty acid feedstock versus a reference catalyst with 22% nickel. The PRICAT 9953^{TM} demonstrates at least equal performance as a result of its higher activity per unit of nickel as shown in *Figure 1b*. Industry can replace their existing 22% nickel fatty acid catalysts with PRICAT^{TM} 9953 without making large modifications to their process.

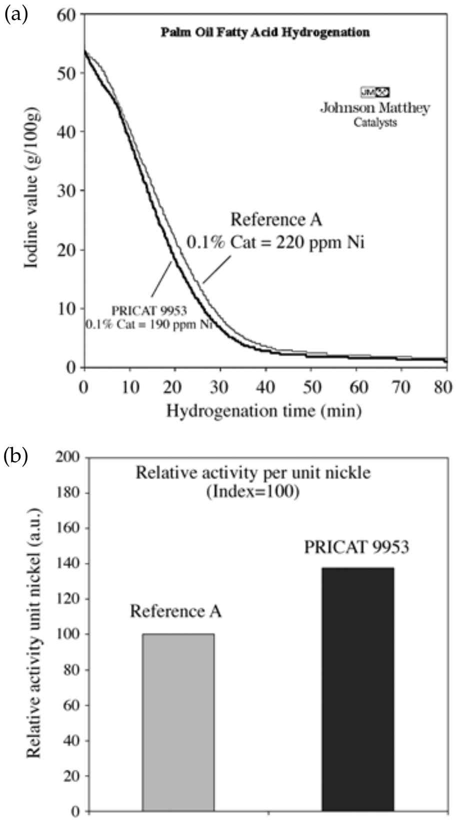

Figure 1. Performance of lower-nickel PRICAT^{TM} 9953 (19%) vs. *a standard-nickel reference catalyst (22%).*

LOWER-GRADE FEEDSTOCK HYDROGENATION AND CATALYST REUSABILITY

There is increased interest in industry to upgrade low quality oils into a range of products, including biodiesel components. For example, waste oils from animal rendering plants and restaurants, as well as oils derived from fermentation processes, are used. Typically, the latter originate from aqueous suspensions and as such can contain high levels of water as well as salt impurities. In other feedstocks of interest, the levels of contaminants such as sulphur, phosphorus, chlorine, nitrogen, free fatty acids (FFA), water, soaps, *etc*., can be high. The catalyst performance in the hydrogenation reaction is directly related to the purity of the feedstock. Purification of oils and fats is becoming increasingly costly, for instance, because of the high energy prices. Distillation of feedstocks with high levels of contaminants has become an expensive operation, and less efficient separation leads to an increased level of heavies/lights, sterols/tocopherols, and water in the oil. Similar arguments apply for bleaching and deodorisation. There are, however, several ways to apply hydrogenation catalysts for poison-rich feedstocks in such a way that the most effective performance can be achieved, so that the cost balance is optimally maintained. This is illustrated in the following application examples.

Application Example 1 – Sequential Dosing for Higher Poison Feedstocks

The most common way of achieving hydrogenation in slurry-phase reactors is through a single dosage of catalyst for each batch of oil. For feedstocks with low levels of contaminants, this is indeed generally the optimal method, but for high level contaminant feedstocks, the mechanism of catalyst poisoning could call for an alternative sequential dosing method, as shown in *Figure 2*. This example permits the hydrogenation of a tallow-derived fatty acid, which contains a high level of sulphur (38 ppm).

A single dosage of 1400 ppm nickel will give a hydrogenated product an end iodine value around 5 g/100 g. In addition, the resulting sulphur content at 9 ppm is still high. These are often values that exceed the specifications of the product. In the alternative sequential dosing approach, 800 ppm nickel are added to the system in the first step. After a given time, a second charge of 600 ppm fresh nickel is added. As can be seen from the graph

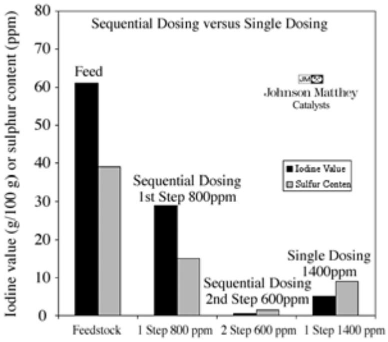

Figure 2. Benefit of sequential catalyst dosing over single catalyst dosing for a tallow-derived fatty acids feedstock with high sulphur level.

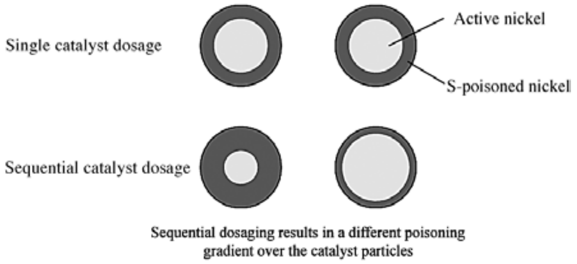

Figure 3. Single catalyst and sequential catalyst dosing mechanisms for feedstocks with high contaminant levels.

in *Figure 2*, the end iodine value (< 1 g/100 g) and sulphur value (< 2 ppm) are much lower than when using a single dosage, although in total the same catalyst amount has been used.

The reason for the observed behaviour is shown in *Figure 3*. When using a single dosage, the sulphur will deposit almost equally onto all the nickel catalyst particles that are present, thereby decreasing its activity. In the sequential dosage approach, most of the sulphur will deposit onto the first charge of catalyst. Although the activity will be affected more than for the single dose approach, the catalyst has a second function in acting as a sink for the poison. With the second charge, the catalyst will be much less affected by the poisons left in the feedstock, and therefore will maintain its activity for a longer time. It should be noted that a sequential dosing approach could be carried out without intermediate filtration, as long as equipment configuration allows for it. Johnson Matthey Catalysts offers different grades of catalysts that can be used for different dosing methods.

Another example relates to the hydrogenation of so-called 'industrial oils', *i.e.* triglyceride feedstocks with high FFA levels that are typically used for technical (non-edible) purposes. Common triglyceride hydrogenation catalysts typically often deactivate very rapidly due to the leaching of the active nickel by the fatty acid components, whereas a dedicated fatty acid catalyst would usually demonstrate too low a hydrogenation activity. This problem can be overcome with PRICAT™ 9936, which is a dual-purpose catalyst that can be used for both triglyceride and fatty acid feedstocks. *Figure 4* shows an example of the hydrogenation of a triglyceride feedstock with 4% FFA using PRICAT™ 9936 compared to a reference standard fatty acid catalyst. The PRICAT™ 9936 shows good performance, and in many cases it can also be applied successfully for the hydrogenation of pure fatty acid feedstocks. This provides the industry the flexibility to hydrogenate different oleochemical feedstocks with a single catalyst.

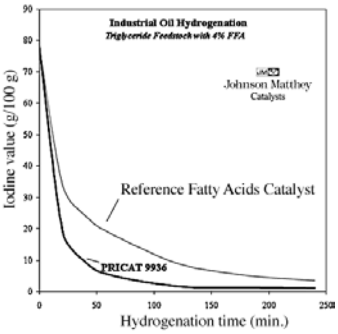

Figure 4. Example of the hydrogenation of a triglyceride feedstock with high free fatty acid level, using PRICAT™ 9936 and a standard fatty acid catalyst.

Application Example 2 – Catalyst Reuse and Filtration

The catalyst's 'initial activity' (activity of a fresh catalyst) is an important parameter for the hydrogenation process, but ultimately it will be the 'productivity' (kilogrammes of fresh catalyst consumed) that determines the actual value of a catalyst to industry. Catalyst reusability (*e.g.* through filterability) and lifetime are important parameters for productivity. Although different catalysts may have similar initial activity, they can turn out to have different productivity, and in even more extreme cases, a catalyst with a higher initial activity may turn out to have a disappointingly low productivity. For example, bringing the nickel content up to 25% may yield a higher initial activity per kilogramme of catalyst added, but this does not necessarily improve the catalyst lifetime, its robustness, and, more importantly, the productivity per kilogramme of catalyst consumed. Selection of the right catalyst for the right feedstock under the right process conditions is therefore critical. How this applies to practical situations is illustrated by the following five cases, for which a simple calculation model was set up to demonstrate the principle.

Cases A-D. A common practice in industry for the reuse of a catalyst is through the filtration of the catalyst after the first hydrogenated batch. The used catalyst is then recycled back to the reactor where its residual activity is used for the second batch. The lower activity of the used catalyst is compensated for by adding a certain amount of fresh catalyst, often referred to as 'topping off' or 'topping up'. The amount of fresh catalyst that needs to be added for each new batch is, among others, determined by the residual activity of the used catalyst (catalyst lifetime) and the filtration efficiency.

In Case A, it is assumed that the fresh catalyst dosage for the first batch is 10 kg, and that the filtration efficiency for the used catalyst is 99% (for simplicity's sake, assumed to be independent of catalyst age). It is further assumed that this amount of used nickel catalyst has a 45% retained (residual) activity of the catalyst as compared to the fresh catalyst. For simplicity's sake, it is also assumed that the decay follows a linear trend. This means that for the second batch 5.54 kg of fresh catalyst need to be added (topped off) in order to obtain the same overall activity as for the first batch. The same top-up mass will be required for the next batches, which is illustrated by the model output in *Table 1*.

Similar simulations have been run for the next three cases, as can be seen in *Table 2*. In Case B, it is assumed that the filtration efficiency has decreased to 95% as compared to Case A, while the residual activity of the used catalyst will be similar at 45%. The catalyst top-up mass increases in this case to 5.72 kg. This agrees with an increase in catalyst consumption of more than 3%.

In case C, it is assumed that the filtration efficiency is back to 99%, but that the residual catalyst activity is only 35% instead of 45%. The top-up mass increases to 6.54 kg. This is an increase in catalyst consumption by almost 18%. Moreover, the catalyst inventory in the reactor will increase substantially during the process, which can result in a much longer filtration time and therefore a longer cycle time (lower production capacity).

In the most extreme case D, both the residual activity and filtration efficiency have decreased to 35% and 95%, respectively. The top-up mass will increase to 6.68 kg, which agrees with a total catalyst consumption increment of 20%.

TABLE 1. CASE A MODEL OUTPUT RESULTS

Fresh catalyst dosed for first batch	(kg)	10
Relative activity of fresh catalyst	(%)	100
Filtration efficiency	(%)	99
Retained activity used catalyst	(%)	45
Top-up mass	(kg)	5.54

	1st batch		2nd batch		3rd batch		4th batch	
	Mass (kg)	Rl. Act. (%)	Mass (kg)	Rl. Act. (%)	Mass (kg)	Rl. Act. (%)	Mass (kg)	Rl. Act. (%)
1st batch	10.00	100.00	9.90	45.00	9.80	20.25	9.70	9.11
2nd batch	-	-	5.54	100.00	5.49	45.00	5.43	20.25
3rd batch	-	-	-	-	5.54	100.00	5.49	45.00
4th batch	--	-	-	-	-	-	5.54	100.00
Total	10.00	100.00	15.44	100.00	20.84	100.00	26.17	100.00

TABLE 2. CASES A-D

		A	B	C	D
Fresh catalyst dosed for first batch	(kg)	10	10	10	10
Relative activity of fresh catalyst	(%)	100	100	100	100
Filtration efficiency	(%)	99	95	99	95
Retained activity used catalyst	(%)	45	45	35	35
Top-up mass	(kg)	5.54	5.72	6.54	6.68
			(+3%)	(+18%)	(+20%)
Catalyst mass in reactor:					
1st batch	(kg)	10.00	10.00	10.00	10.00
2nd batch	(kg)	15.44	15.23	16.44	16.18
3rd batch	(kg)	20.84	20.19	22.81	22.04
4th batch	(kg)	26.17	24.90	29.11	27.61

These four cases demonstrate that initial activity is only one of the critical parameters in catalytic hydrogenation. When reusing a catalyst, it is equally important that the catalyst can maintain acceptable residual activity and filtration characteristics during a full process run. Also, smaller catalyst particles may give a higher initial activity, but the loss of catalyst mass during filtration may be high, which means that the required top-off mass will be higher (and similarly overall consumption).

Case E. This case relates to the principle of collecting enough used catalyst from the filters until there is enough to do a single batch hydrogenation with it. Imagine that if two batch hydrogenations were run with fresh catalyst, and this is followed by a batch with the collected used catalyst from the first two runs, then the overall fresh catalyst consumption is equal to 67% per batch (*Table 3*). On the other hand, if three batch hydrogenations were run with fresh catalyst, followed by one batch hydrogenation with the collected used catalyst from the first three runs, then the fresh catalyst consumption is higher, *viz.* 75%.

Again, this example illustrates the necessity of looking at the overall hydrogenation process. This includes not only the initial activity of the fresh catalyst but also the performance of the catalyst during filtration and its ability to maintain a certain level of activity over a prolonged period. Johnson Matthey offers catalysts with high robustness that can help improve productivity.

NEW PROCESSES: FIXED-BED NICKEL CATALYSTS

Fixed-bed nickel catalysts can be widely applied in the oleochemical industry as they offer good process economics and contribute significantly to sustainability. Johnson Matthey offers its HTC™ nickel catalysts for use in the manufacture of products from renewable sources. The HTC™ catalyst range consists of alumina extrudate supports (1.2 and 2.5 mm) on which various loadings of nickel can be dispersed. The use of HTC™ catalysts in oleochemical applications is illustrated by the two following application examples.

TABLE 3. CASE E

Fresh batches	Collected used batches	Total hydrogenated batches	Fresh catalyst consumption per batch
2	1	3	67% (=2/3)
3	1	4	75% (=3/4)

Fatty Alcohol Polishing

During the synthesis of fatty alcohols, undesirable impurities can be formed by side reactions; for example, aldehydes (carbonyls) and unsaturated colour bodies, which can result in a bad smell and unwanted colour properties. Fatty alcohol polishing is applied to remove primarily carbonyl groups from the product through hydrogenation, as well as to remove colour bodies (Suyenti *et al.*, 2007). Sodium borohydride ($NaBH_4$) can be used for the selective reduction of carbonyls, but it needs to be added in excess, and additionally its use results in the formation of by-products. These by-products need to be washed out of the alcohol product, thereby generating a waste as well as having the possibility of leaving salts in the product. A more sustainable way of carbonyl reduction, by a low-investment ‘end-of-pipe’ solution, is through catalytic hydrogenation that yields a low-carbonyl and water-white product, without continuous waste formation.

Typically, nickel-based catalysts are used in these reaction systems where limited poisoning of the active metal surface takes place. Although high-nickel tablets (>50%) can be used for this purpose, lower-nickel extrudate catalysts have demonstrated excellent performance for these selective hydrogenation reactions. Johnson Matthey’s HTC™ nickel extrudate catalyst range for fatty alcohol polishing applications contains less than 27% nickel, depending on the specific application. Apart from the difference in metal costs, other advantages are given below and in *Figure 5*:

- highly dispersed active metal phase, giving high metal surface area;
- narrow pore distribution; wide pore diameter for high diffusivity;
- low-acidity support; side reactions minimised;
- high physical strength, low attrition index;
- trilobe shape, with high external surface area;
- dense or sock loading methods possible for charging the reactor;
- high void space, minimum pressure drop;
- enhanced activity for reduced operating temperature;

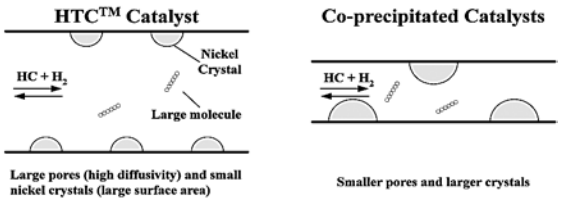

Figure 5. Schematic representation of a lower-nickel HTC™ catalyst pore vs. *a higher-nickel co-precipitated catalyst.*

- longer catalyst life;
- low operating temperature favouring high selectivity; and
- channelling in reactor minimised.

The HTC™ nickel extrudate catalyst can be supplied in reduced and passivated form, which is an additional benefit because it will allow for mild activation conditions of the catalyst on-site (< 200°C).

A typical example for a polishing unit is shown in *Figure 6*. The numbers in this figure are merely indicative, and the real operation conditions need to be calculated for each specific case. The high-carbonyl fatty alcohol is mixed with hydrogen and led over the HTC™ extrudate catalyst bed. The reactor effluent is led through a 'flash drum' separating the liquid low-carbonyl product from the gaseous hydrogen, which can be purged or recycled to the reactor.

Methyl Ester Hydrogenation

Apart from its wide use in biodiesel applications and as an intermediate for fatty alcohol production, methyl esters can be used for the production of MES. Although the MES market is in its early stage of the growth, Frost and Sullivan (2004) estimate that the unit shipment of MES will reach 126.5 thousand tonnes in 2012, growing at a compound annual growth rate (CAGR) of 30.6%. MES are of general interest because they are derived from renewable oils and are relatively inexpensive. Moreover, they possess excellent detergent and environmental properties. MES is produced through the sulphonation of methyl esters. As double bonds in the methyl ester interfere with the reaction, a low saturation level (low iodine value) is highly preferable, also because of the better resulting colour properties. This requires extensive refining, which can be a costly operation. Catalytic hydrogenation is an economic and sustainable alternative (Trivedi Group).

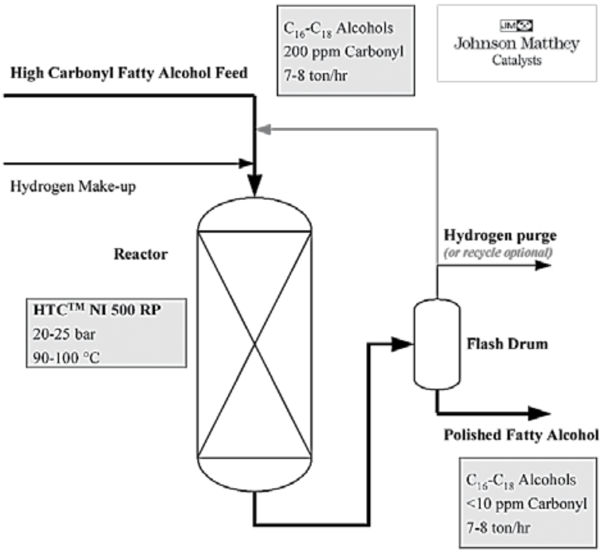

Figure 6. Example of a process layout for fatty alcohol polishing.

As in the case of fatty alcohol polishing, HTC™ nickel extrudate catalysts prove to be a sustainable and successful way for the selective hydrogenation of methyl esters. The double bonds are readily hydrogenated, whereas the ester link in the molecule is unaffected due to the relatively low operating temperature. Very low iodine values can be obtained in this way. The process layout can be similar to the one for fatty alcohol polishing as depicted in *Figure 6*, but for feedstocks with higher iodine values one may opt for a two-stage unit with an intermediate quench to accommodate for the reaction heat generated.

Also for biodiesel applications it would be beneficial to reduce the content of unsaturates in the methyl ester product, as they are prone to oxidation reactions. Removal of the double bonds leads to a higher oxidative stability, thereby giving higher value to the end product.

CONCLUSION

The examples presented in this article on novel catalytic solutions for existing and new oleochemical processes demonstrate that catalysts play an important role in the manufacture of sustainable chemicals derived from oils and fats. Although catalyst costs are marginal compared to the total variable costs, they are key to the production of a wide range of oleochemicals. As a result of their intrinsically sustainable nature, catalysts (which are not used stoichiometrically in chemical transformations) should therefore always be considered for chemical reactions.

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