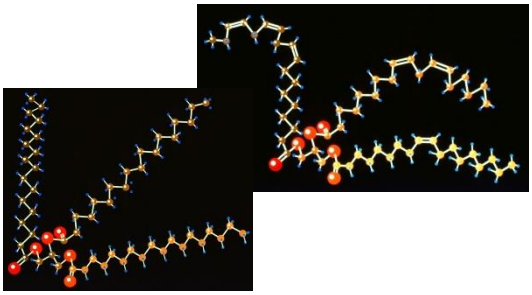
PMI-Technology Sdn Bhd (568062-K)

FILTERING THROUGH THE NEWS No. 21



Date : 08-09-2015-rev 2

Attn :

To whom it may concern;

FILTRATION OF HYDROGENATED VEGETABLE- ANIMAL OILS OR FATTY ACIDS /ESTERS (OLEO CHEM);

With reference to the papers published on this issue before we would like to send you our latest revision where the latest changes and additions have been included. The main change has been the change from hydrogenated to interesterified and fractionated products based on health issues (Trans isomers), public opinion and the tendency to look for non- chemical food processing . Terms like soft degumming , CO2 extraction and enzymatic interesterification have to a certain level blinded peoples mind. The perception certainly played a role in the way the industry looked at alternative process options.
It was a noticeable change in the processing of edible , vegetable and animal oils and was not restricted to refining & bleaching only . Also the hydrogenation of fatty acids, esters, monomers and methyl esters was greatly influenced by the changes we saw coming.
The Filtration of catalyst has always had the attention of the industry because the catalyst was the most important cost in the process and its reduction or possible re-use became a major driver in the quest for better and more economic catalyst and/or filter systems.
In order to get acquainted with the process we herewith give you a little background .

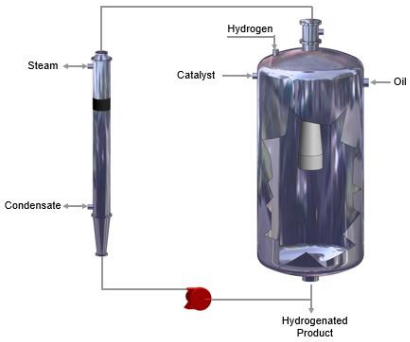
BACKGROUND (hydrogenation) ;

When more than 150 years ago Emperor Napoleon the Third became concerned about the strong rise in the price of butter, He asked inventor Hypolyte Mége Mouries to develop a product to replace real butter with a product with a longer shelf life. This took place in 1869 and in 1889 the name margarine was introduced to show the difference between butter and the substitute spread. It was Wilhelm Norman who in early 1906 introduced the hydrogenation of edible oils & fats. Since it's invention more than 100 years ago, the hydrogenation of oils and fats has proven to be a useful tool in the manufacture of edible and technical products made from natural oils and fats. The hydrogenation of oils and fats has grown into a very versatile process that can be used to give edible oils and fats the desired properties in terms of fatty acid composition, melting characteristics and oxidative stability.

Improved catalyst performance in combination with process improvements have resulted in steady progress in product functionality and process economics. From a nutritional point of view it seems that development has been rather turbulent, especially in recent years.

BSE in animal fats ,GMO oils, the introduction of fat replacers/cholesterol cutting products and the “trans” issue have been active topics of discussion. Labelling laws in Europe and in America have not been the reason for all the changes but certainly have contributed greatly .

In the past hydrogenation was the most important process step to modify liquid oils into solid fats used in margarine, confectionary fats, CBE & CBS product and other products. This paper will also cover the hydrogenation of oleo-chemical products



The hydrogenation or “hardening” process for edible oils & fats can be either batch or continuous. Most commercial operations require changes in oil feed stock and in some cases alterations in the process parameters, which are difficult to handle in continuous systems. For this reason the batch process was preferred and most commercial batch designs operate a converter type “dead end” autoclave or the “loop” reactor . At the moment the oils & fats hydrogenated for edible applications are fully hydrogenated followed by interesterification (Chemical or enzymatic). This can result in continuous or semi continuous hydrogenation.

What where the main objectives of hydrogenation;

* To enhance the stability of easily oxidised poly unsaturated components of the oil.
* To modify the melting properties of the oil to allow more convenient usage like chocolate that melts in the mouth and not in the hand or margarine and semi solid shortening fats.
* Full hydrogenation to prepare for interesterification.

A more gentile way to process the oils and get to the required IV values is the fractionation of oils like Palm ,Palm Kernel , Butter oil , fish oil , shea oil , etc. This requires a different approach and filter type or system . A special “filtering through the news” no 18a is available on this subject.

Main difference; fractionation is fully reversible and hydrogenation is not.

The final selection of the process and the catalyst filters used is a matter of experience-, personal preference, product hydrogenated and the engineering company involved.

TYPE OF FILTERS /SEPARATORS USED:

A) Filter press or Plate & Frame type filter.

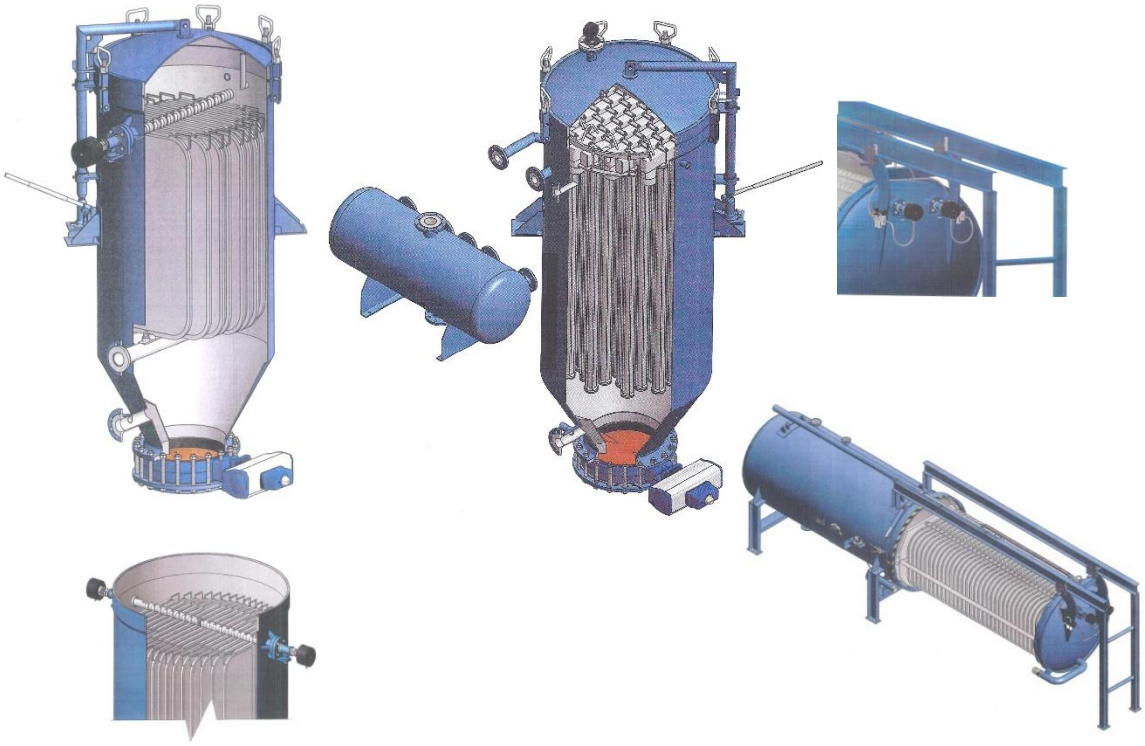
This filter type was historically found in every oil processing plant, but due to housekeeping , labour & maintenance, yield and residual nickel in the filtered product, the filter has more or less been phased out of most processing plants. It's main advantage was that it could handle batches but many disadvantages have made the Plate & Frame filter type redundant.

B) Centrifuge.

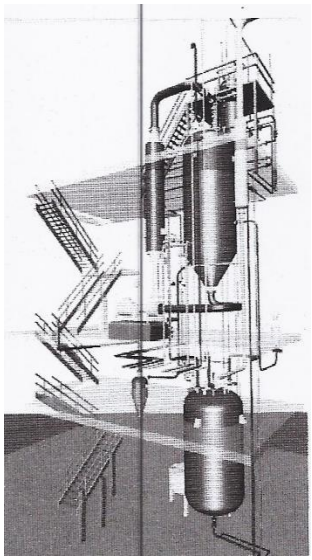
Only limited in use, since the machine can only be used for bulk removal of catalyst and further reduction still requires further filtration. Wear of the catalyst due to centrifugal forces results in the mechanical break up and creation of fines in the clean oil. Mechanical wear and tear of the centrifuge was another reason to look for other options. The advantage of the centrifuge is the fact that it is continuous .And as I mentioned before if a centrifuge could give you the requested residual solids (in this case nickel) it would be the best choice to make

C) Pressure leaf type filters.

D) Pulse Tube type filters.



The first and important decision we have to take is a choice between the pressure leaf type filter which has historically been used and where still a lot of systems are successfully in operation and the more recent RP pulse type filter. The search for a better i.e. more economic system had as main reason the need to handle dry cake discharge applications where only very little cake had to be discharged . We used experience gathered in other catalyst filter applications and applied this to the oil & fat process .



“HOT” FILTRATION:

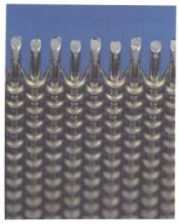
There is a general tendency to filter the catalyst as hot as possible but we have to consider the danger in doing so. It will have great viscosity and thus filtration rate advantages to filter hot (180-220 degrC) but it will limit the type of filter media used in the RP Pulse filter. Only sinter bonded stainless steel (Mott, Fuji,Pall,etc) or full teflon cloth can be used.
The process will become easier since no heat exchange is required.

The std filter temperature now on leaf filters is 80-110 degrC and this will also limit the risk of spontaneous combustion.
With the RP Pulse we have access to the high temp filtration options but we should handle this with care .(See enclosed diagram)

	Hot Filtration	Plate & Frame Filter	Pressure Leaf or Pulse Filter
Max. Operating Temperature [^oC]	220 ^oC	100 ^oC	120 ^oC
Flow Rates [l/hm2]	<1500	<500	<600
Precoating	No	Option	Option
Precoate Material in Spent Catalyst	No	Yes	Pulse Type no Leaf Type yes
Heel Filtration	Yes	No	Pulse Type yes Leaf Type no

PULSE "RP"FILTERS VERSUS "PL"PRESSURE LEAF FILTERS:

Based on the process conditions we can offer and use both leaf filters and back wash filters The application with it's limitations and requirements is the main reason for the choices made and we have tried to make them understandable.
The classic vertical tank vertical leaf type filter only has very little variation and is available as slurry discharge (WC) model , as dry cake discharge model (DC) or in those cases where we want to re-use the catalyst cake as a W&DC model. DC when the catalyst cake is exhausted and waste but the extra oscillating sluice header (WC) will allow for slurry discharge the cake with minimal exposure to air and moisture that would kill the catalyst activity. When batch processed the PL filter will have to deal with a full filer volume as "heel "that needs to be processes separately.
The leaf filter will be equipped with full stainless filter elements and he filter septum is filter screen like the PZ80S (see "filtering through the news" no 16).



Screen will require between 0,5- 1 kg dry solids per sqm to obtain clarity.

Textile

The Pulse (RP) type filter is available in three(3) versions i.e.

- As Main process filter. RP(D or W)
- As polishing or safety filter. RPP(W)
- As Heel filter. RP heel (D&W)

There is a fourth version, " the continuous thickener", but this is only used for very special applications.

In making the comparison It should be remembered that a PULSE (RP) filter will have much more filter elements than the alternative leaf filter (Pulse 30 m² for 20 mm cake thickness has 60 tube type elements while the PLV Vertical tank, vertical leaf filter has max 15 leaves for the same area which makes operation and service a lot easier. The filter septum is a filter cloth which will require much less solids to obtain clarity but is easier to damage.

We differentiate between the following options;

A) **FULL HYDROGENATION (mostly followed by interesterification)**
B) **PARTIAL OR SELECTIVE HYDROGENATION.**
C) **FRACTIONATION.**

In this paper we will concentrate and limit ourselves to the actual removal of the catalyst from the oil or oleo chemical and we will try to also indicate which filter type should be used where.
As we mentioned before in our "bleached oil filtration " special paper the particle size distribution is of significant influence on the bleaching itself but also on the filtration performance . In the past it was common to find the best possible clay with very fine particles that was optimal for the bleaching step but shear impossible to filter.
In the old days i.e. 30 years or more ago it was common to compensate this bad filterability of the clay by using a pre-coat and a body feed.
Now it is common to focus on filterability
This resulted in a range of bleaching clays like;
-TONSIL OPTIMUM FF by Sud Chemie (Clariant) where FF = FAST FILTRATION.
-FILTROL 105 SF by Engelhard (BASF) where SF = SPEED FILTRATION
-OIL DRI Select FF = FAST FILTERING.

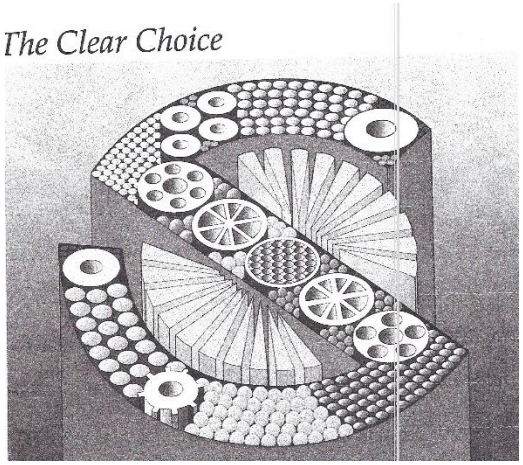
In catalyst filtration the nightmare is to find the best filtering catalyst but then discover it is not active or selective enough. The opposite however is to find the best catalyst for the job but it filters badly.
For the filtration of hydrogenated oil & fat we have to consider other important issues like re-use of catalyst (if possible) and a much lower solids load (in general;

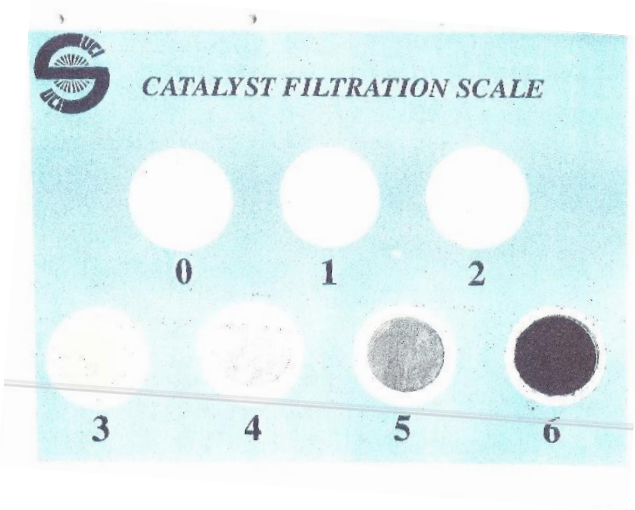
catalyst dosage in the range of 0,1 kg per ton of product (=0,1 %)and bleaching clay 1-2% dosage.
Re-use in fatty acid applications is only possible in case of a precious metal catalyst like Palladium or platinum on carbon . Few installations are build and operate this way but it has been considered to expensive.

In the many tests that where conducted with most of the leading catalyst suppliers as there where and are;

- Engelhard / Harshaw now BASF.
- Unichema catalyst now Johnson Matthy.
- Sud Chemie catalyst, Girdler now Clariant

The most common filtration test used by the industry was a test filter method published by United Catalysts which became at one moment the industries standard.(See enclosed info)
Many discussions were also held over the amount of solids measured. Did the solids include the nickel in solution ???





We differentiated between the solids as solids in the oil without the metals that went into solution and had to be treated with an acid (citric acid) to solidify these solids first by turning them into metal soaps. These soaps had a negative influence on the filter performance. The process therefore was split into two filter applications called catalyst filter and post treatment filter In the US one could run into the name “Black Filter” and “White Filter “.

The **black filter** was filtering the hydrogenated oil without the addition of citric acid with the main target to protect the catalyst from being poisoned by the acid. If the spend catalyst can also be protected from too much exposure to oxygen and/or

moisture it could be re-use under the correct conditions. It was mentioned that even Under the best conditions the filtered oil would still have up to 2 pp nickel or more.

The **white filter** filtered the oil once it was mixed with citric acid to solidify nickel into residual nickel soaps. These solids where substantial more difficult to filter and systems where developed where we called it post bleaching/post treatment with filtration result of <0,2 ppm residual nickel .
In this post bleaching the oil was mixed with a little bleaching clay which acted as a filter-aid and ensured that a relative high flow rate could be achieved.
In very old installations we saw the oil being mixed with citric acid crystals which where pre-coated on a horizontal leaf filter with filter paper. The short contact time between the citric and the in oil dissolved nickel would bring the nickel soaps out and where trapped into the filter paper.

Cuno had a paper filter sheet product called Zeta Plus that was sold on the assumption that the zeta potential would give additional help.

In selecting the correct system one can choose from the following options;

EDIBLE OIL & FAT:

Once through system where the catalyst is used only once but we will use a minimum of the most active and selective catalyst to achieve our goal. Several batches can be filtered before the filter has to be cleaned.

Bleed & Feed system where after every batch we will remove 10-20 % of the spend catalyst and replace it by fresh catalyst. This way we keep the selectivity and activity at level but generate more cake which has to be considered.

Over dosage of catalyst. In this option the plant is overdosed with catalyst to compensate for the loss of activity / selectivity every batch. After the set amount of batches have been processed the spend cake is wasted’

The last system to mention is **the Cargill system** where the catalyst is re-used only once and from there it is discharged as spend cake.

He simplest is the once through system because we don’t have to consider the mechanical break down of the catalyst into smaller particles which will be the result of catalyst re-use. The type of reactor (Dead end or Loop) also contributes to the rise of catalyst fines.

With the increased awareness of environmental “green” production which has grown under the eye of public opinion most refiners would not like to be linked to waste scandals. On top of this political debate we also have the consider the rest value of used catalyst i.e. scrap nickel value.
This rest value was the reason for process considerations where the nickel content in the spend cake was as much as possible kept the same as in the original catalyst and only the carrier material (DE or Alumina) was unchanged after use. The use of additional solids like filter aid should be avoided where possible.
If filter aid needs to be used a choice can be made from the available three most used filter aid options i.e.;
DE = Diatomauthous earth (=fossil ,kieselguhr) by Celite Corp.
PERLITE= volcanic glass like structure by Dicalite Corp.
CELLULOSE= wood pulp by Rettenmeyer Corp.

WHICH FILTER TO USE IN WHICH APPLICATION:

PULSE FILTERS VERSUS LEAF FILTERS

Based on our experience and the client preference we can offer both leaf filters and back wash filters from our extensive filter program.; The application is our mean reason for the choices made and the choice can be as follows. .
The Pulse (RP) type filter is available in three(3) versions as we mentioned before ..

- **Main process filter. RP(D or W)**
- **Polishing or safety filter. RPP**
- **Heel filter. RP heel D/W**

The filtration of hydrogenated EDIBLE OILS &FATS or the filtration of hydrogenated of fatty acids ,esters / methyl esters, monomers, dimers i,e OLEO CHEMICALS is in principle the same.

When sizing the filters it is only important to know whether it is a continuous process or batch-process. Important is also to know if re-use of the catalyst is considered

The main process RP PULSE TYPE filter is W*wet cake discharge, D*dry cake discharge or both W/D.

The tubular filter elements can be made in all stainless wedge wire design , wire mesh screen center core , full PP ,PVC or PVDF and all are cloth covered. In the catalyst removal application we will use the wedge wire core design . This design has obvious advantages over oval shape elements (Cricket) in the market (for Delta P the best shape is round tubular elements with seamless cloth while oval shape elements tent to become flat in filtration mode or round in backwash mode while the cloth will be supplied with a seam). The round elements by the way they are positioned in the filter tank will require a bigger tank diameter if compared with the non round element shape but this does not justify to abandon all the other advantages. Since we offer a wide array of filter types and models which includes both the back pulse model and the leaf filter models of which the Vertical tank , vertical leaf is only one . Based on this we can be neutral and objective in our recommendation and choice .Based on experience, the application and the commercial effect we would select the best possible choice. Hydro catalyst filters are sized on max 10-15 mm cake thickness

When using the RP Pulse filter as the main process filter it will be important to know what the process criteria are but the main cycle will always consist off the following process step;

RP PULSE FILTER CYCLE

- Fill filter. Re-circulation to obtain clarity. No or only very little pre-coat and /or filter aid required depending on solids in feed.
- Filter the batch or cycle.

Depending on dry or wet cake we now continue ;

AS DRY CAKE “D” model;

- Heel drain and heel filtration if entire batch has to be processed.

NOTE:Complete filter volume i.e. heel can be processed on pulse filter we recommend however to filter max 50 % of the main filter volume(heel) and filter the remainder 50 % on separate heel filter.

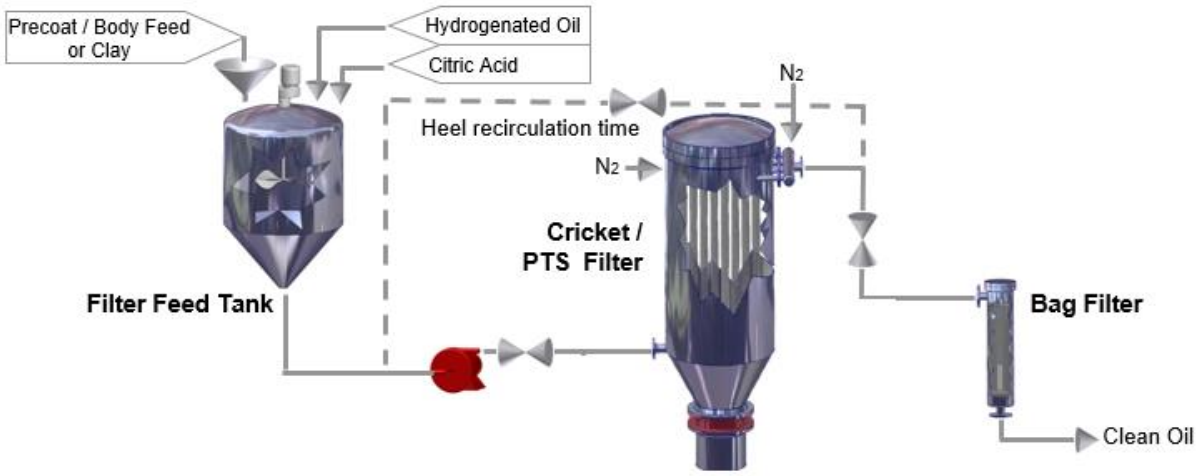
- Dry the filter cake (wash the cake if application required).
- pulse dry discharge the spend cake
- Stand -by

AS WET/SLURRY CAKE MODEL “W’;

- After completion of the filter cycle the filter elements are pulsed with either gas or clean liquid in a full filter tank. The entire slurry is drained from the filter and goes back into the process.

Stand-by

A typical P&ID is enclosed.



PL V LEAF FILTER CYCLE

- Fill filter.
- Re-circulation to obtain clarity.

  NOTE; With a leaf filter we need minimum 0,5-1 kg solids per sqm filter area in order to obtain clarity. Suppose process has 10 mt batch to be filtered in 90 minutes max. The filter we need will be approx. 20 sqm and based on the minimum required solids we need 10-20 kg solids just to get clarity. The entire hydrogenated batch will hold 0,1 kg catalyst per ton i.e. 10 kg which is not enough to obtain clarity (in a reasonable time frame).

- Filter the batch or cycle.

Depending on dry or wet cake we now continue ;

AS DRY CAKE “D” model;

- Heel drain and heel filtration if entire batch has to be processed.

  Note: Complete filter volume is heel and a separate heel filter is required to filter the heel

- Dry the filter cake (wash the cake if application required).

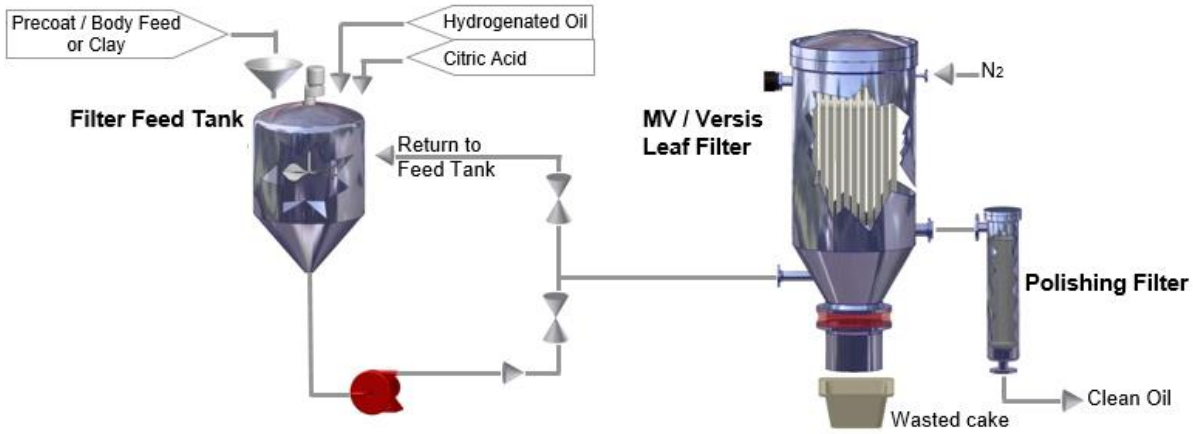
  Dry discharge the spend cake by vibration (minimum cake weight is required in order to avoid the whole building is vibrating but the cake will no be released from the leaves)

- Stand -by

AS WET/SLURRY CAKE MODEL “W’;

- After completion of the filter cycle the filter heel is removed from the filter (unfiltered) under N2 pressure. The spend filter cake is sluiced (washed) off the leaves by pneumatic operated Oscillating sluice header and the catalyst slurry can be reused stand-by

A typical P&ID is enclosed.

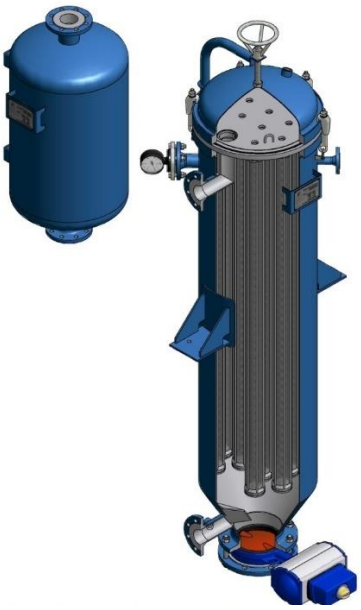


RP POLISH PULSE FILTERS;

The use of RP PULSE filters as polishing / safety filter has become the industries standard . With reference to the many questions asked about the reason and justification for utilization of the back wash type RP PULSE W type polish filter we like to comment as follows.

When considering the Pulse polish filter we have at least four (4) good reasons to change from a disposable element filter (disposable bag or disposable cartridge).

1. The disposable elements cost money to buy.
2. The replacement of disposable elements will require operator time to change the disposable element.
3. The disposable element is soaked with oil product and when thrown away it is considered a loss. The change of disposable element is also considered a housekeeping problem.
4. The disposal of disposable elements is considered industrial waste and will be charged as such.



The RP PULSE type polishing filter has become a standard used by refiners and engineering companies and is used to replace or avoid the use of consumables used in Bag, Cartridge or paper sheet polishing filters. The pressure on cost and waste has been the main trigger in the implementation of this filter type by many in the industry but quality issues, maintenance i.e. labor have also been seen as a big motivator to make the change.
In most cases we will install only one filter to act as polishing//police filter and since this is a police/safety filter we only need one (during cleaning 30-60 second's the filter is by passed).
In the range designed by us to cover the whole range of capacity's have build PULSE polishing filters ranging from 2,4 to 22 m² filter area and in fact several big edible oil refiner groups like ADM/ WILMAR , Bunge, Cargill, De Smet, IOI, Alfa Laval, Oiltek ,and many others have standardized on this filter model for all their plants world wide .

The sequence is more or less as follows;

A) Fill and feed;

The RPP PULSE polishing filter is fed with oil from the main bleaching filters and is merely mend to be used as a police filter that ensures that oil is not contaminated with residual solids/ clay from main bleaching filters. Feed is directly from the main bleach filters or from a metering tank with separate feed pump.

B) Filter cycle;

The filtration cycle is based on both time and Delta-P (whatever comes first). The first and primary rule is the time. The timer is set for 4, 6, 8 or more hours (to be set and tested during start up)and if within the set time frame the Delta-P will reach the x set 1,5-2 bar Delta-P this will take over and the filter is cleaned. In most cases the filter is by-passed during this short cleaning cycle.

C) PULSE/BACKWASH Cleaning;

When the filter has reached the moment of cleaning we stop the feed to the filter. At the same time we stop the filtrate outlet form the filter. To pressurize the filter we open the N2 feed to the filter (on the filtrate side of the filter elements) . When the pressure has build up and reached 1,5-2 barG we open the bottom slurry cake discharge valve and a instant pulse will back pulse the elements , remove the accumulated solids form the filter tubes and the slurry is forced out of the filter back to the process

(Back to catalyst make up tank, bleacher, slob oil tank ,etc) . After 15-30 (small filters) or 30-60 seconds (big filters) seconds the filter elements are clean and the slurry has left the filter. This is when the filter is ready for the next cycle ,

D) Fill filter and continue polishing process.

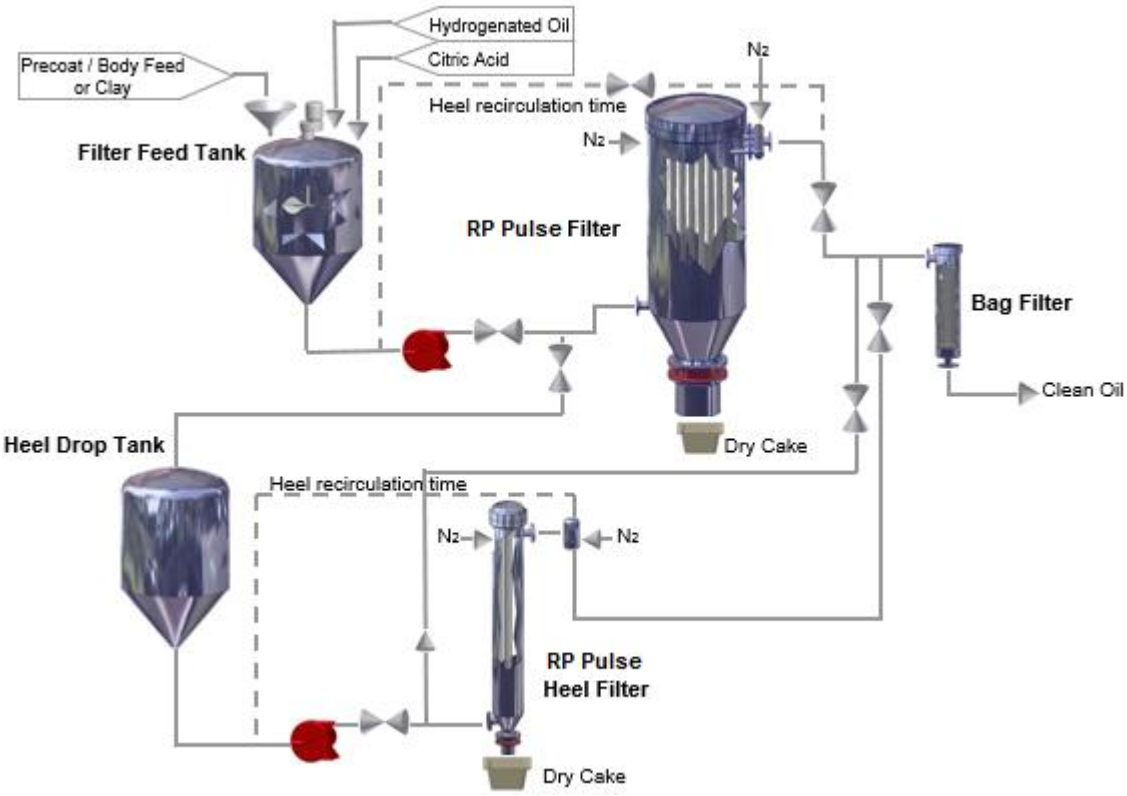
After the filter is pulse cleaned and the slurry has been removed from the tubes and form the filter we will close the N2 feed ,close the cake/slurry discharge valve , (open the vent is option), open the filtrate outlet line and open the feed to the filter. In most cases the oil leaves the filter from the filtrate outlet and is directed towards the further processing. In some cases the filtrate is for 30 seconds re-circulated back to the feed tank to ensure optimal clarity.

he sequence is rather simple and uncomplicated. For bleached oil capacities up to 2000 mt we can offer only one filter with 22 m² filter area . It is however important to understand that the filter will have to be by passed during cleaning .If the client wants to have the security of filtration at all moments we need more than one filter and each filter will need a feed pump. Like in some big capacity refining and bleaching plants for 3500 mt/day we have 3x RPP and there are always 2 filters on stream and the third filter is cleaning or stand by.

HEEL FILTRATION

In applications like hydrogenation it is important to filter the entire run /batch of a certain product without any heel left (zero contamination). The leaf filter is not capable to handle this heel and in most cases this in not required either . When we however have to ensure that the entire product volume is filtered before the next filter run is made (no contamination between the batches)we offer the special RP PULSE heel filter.

This filter is sized on the basis of the heel (residual main filter volume) to be handled in max 1 hr.



OLEO CHEMICALS (FATTY ACIDS, ESTERS , MONOMER) HYDROGENATION:

Most of what is mentioned in the previous descriptions is true for the hydrogenation of oleo chemicals i.e. fatty acids as well. The only great difference is that there will not be a change of feed stock and where the edible hydrogenation is very often a batch process that allows 60-90 minutes for the actual filtration time of the batch, the fatty acid/oleo hydrogenation is often considered a continuous process i.e. no change of feed stock..
The nature of the feed stock also does not allow re-use of catalyst (Ni) and only when precious metal catalyst are used, a possible re-use might be considered. There will also be more nickel in solution which mainly will be recovered at the distillation step where it will be recovered as sludge.
The use of filter-aid will be avoided or minimized to maintain a high Ni contend in the spend catalyst.(reduce oil loss and minimize disposal cost)
The actual chemical composition , process temperature and experience have shown that the gasket material used in this process should be mainly VITON.
Both process leaf and process tube/cricket filters are used whereas the RP Pulse type filter is nowadays the most common filter used. Recent references at more than

50 plants using technology by Lurgi , De Smet,, Crown/Skett,CMB,Lipico and many others are proof of our expertise.
NOTE: Catalyst filter applications can also be found in sorbitol , lactitol, and other non oil or oleo related applications.

SIZING & SELECTING;

When a RP PULSE filter is selected the filter is sized on max 10 mm cake and 400-450 kg/m²/hr flow-rate. Preferably no or only very little filter aid is used. No pre-coat
When a PL vertical leaf filter is selected the filter is sized on max 15-20 mm cake and 350-380 kg/m²/hr flow-rate. Since a filter screen with 80 micron retention is recommended we would pre-coat with 0,5-1 kg/m²/cycle pre-coat material and depending on type and percentage of nickel used we would recommend up to 0,1-0,15 % body feed.
USUAL CATALYST IS ADDED AT NO MORE THAN A USUAL 1-1,5 KG PER TON.

After the cake is formed the spend catalyst cake is dried and wasted. It is common to have 8-10 mm i.e. 4-5 kg spend dry catalyst cake / m²/cycle (no filter aid) on a RP PULSE filter. For a PL leaf filter this is 12-15 mm i.e. 6-8 kg spend dry catalyst cake / m²/cycle but this is based on all solids i.e. catalyst , pre coat and body feed (if necessary).

All electrical components Intrinsically safe EEXiA II CT4 .
The spend cake after blowing with N2 at 0,12-0,15 nm3/m²/min for 15-20 minutes will have 30-35 % residual product in the spend cake based on the AOCS petroleum extraction method test..

SUMMARY

The chemical process of hydrogenation and especially selective hydrogenation is approached differently now due to the world wide issue of “Trans” and the supposed influence on health. More fractionated products are used and interesterification has become more popular. When a product is going to be interesterified , a full hydrogenation before this step is the most common process.

- Leaf- and Pulse tube type filters have become standard equipment in most hydrogenation plants since they operate with a closed vessel and thus avoiding contact of oxygen / moisture with both catalyst and hydrogenated product.

- Leaf - and pulse type filters allow once through and one time use of catalyst or re-use of catalyst in the same filter.

- If compared to chamber filter presses or plate & frame filter presses the Leaf and pulse type filters can be a fully automated part of the process and housekeeping is greatly improved.

- The use of “Heel” type RP pulse filters make complete filtration and recovery of the entire batch possible.

- The use of “POLISH” type RP pulse filters has become standard practice and for described reasons it is the best way to safe money and improve plant performance

With this write up on the filtration of catalyst from hydrogenated oils/fats and fatty acids we try to summarize the latest developments and advantages of leaf / pulse type filters used in this application.
We are aware that we are far from complete on this process.
In case of any specific questions related to the filtration of catalyst from oils, fats or oleo chemicals please contact the PMI Sdn,Bhd office or your local representative

Personal regards,

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Lochem , FGV rev 2 / 08-09-2015