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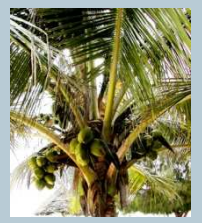

How to add value to By-Products from Edible Oil Refining

Mario Bernardini

Istanbul Advanced Oils & Fats Processing

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Our company C.M. Bernardini with 50 years of experience in the world of oils and fats, has realized several units that are described in this presentation. Many of our customers have expressed their intention to add value to their refinery By products especially when oils and fats prices are increasing in the international market.

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THE IMPORTANCE OF WASTES

- Biodiesel produced from wastes will count double by 2010 in Europe.
- This has been already implemented in Holland and France.
- This has increased dramatically the value of Used Frying Oil and soapstock fatty acids.

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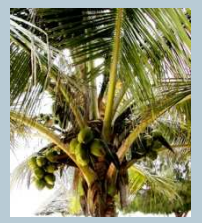

By-product obtained from Edible Oil Refining:

- Acid Oil from Soapstock
- Fatty Acids from Physical Refining
- Bleaching Earth from Bleaching
- Waxes or stearine from Winterizing

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What are the best ways to add value to these products in order to obtain oils and fats to be processed further and also to reduce the quantity of waste?

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Major Process to be adopted:

- Esterification with Glycerol of Acid Oil or Fatty Acids coming from Physical Refining
- Esterification with Methanol of Acid Oil or Fatty Acids coming from Physical Refining
- Acid Oil treatment
- Splitting and Distillation
- Solvent Recovery

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PROCESS	PRODUCT OBTAINED
Esterification with Glycerol	Neutral oil
Esterification with Methanol	Methylester
Splitting-Distillation	Fatty Acids
Acid Oil Treatment	Better quality of acid oil
Solvent Recovery	- Crude oil from bleaching earth - Oil from waxes

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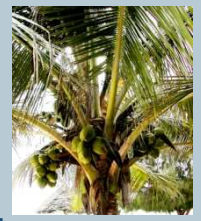
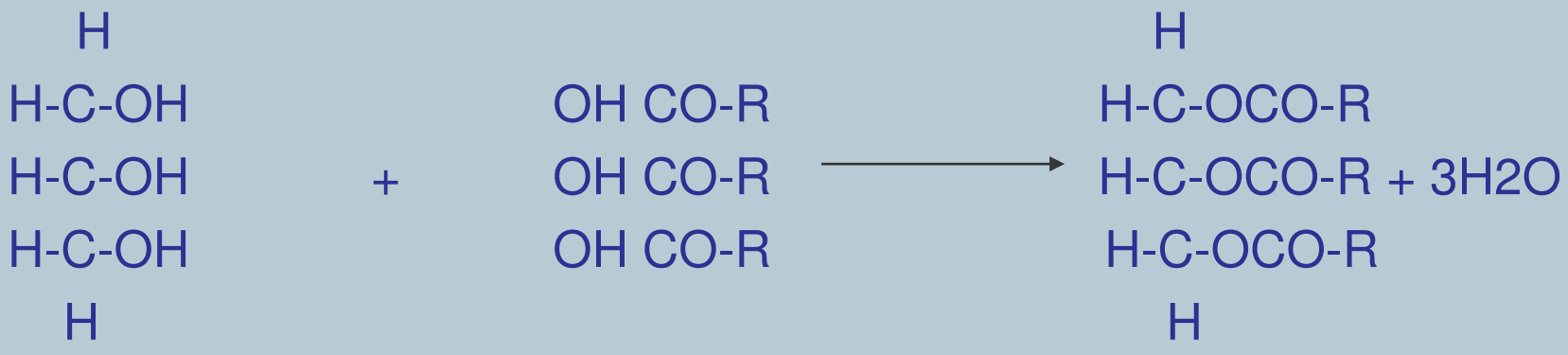


ESTERIFICATION WITH GLYCEROL

It is exactly the reverse of fat hydrolysis or fat splitting.

Following reaction takes place between glycerol and fatty acids.



Where R is the radical of a Fatty Acid

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ESTERIFICATION CONDITIONS

- High vacuum during reaction
- Temperature of the order of 200 – 220°C
- Intimate contact between Acid Oil – Glycerol and proper cathalyst.

The presence of cathalyst is important to speed the reaction and also to lower the reaction temperature.

The glycerine normally used for this process is the commercial product with 98% concentration.

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FINAL PRODUCT AFTER ESTERIFICATION

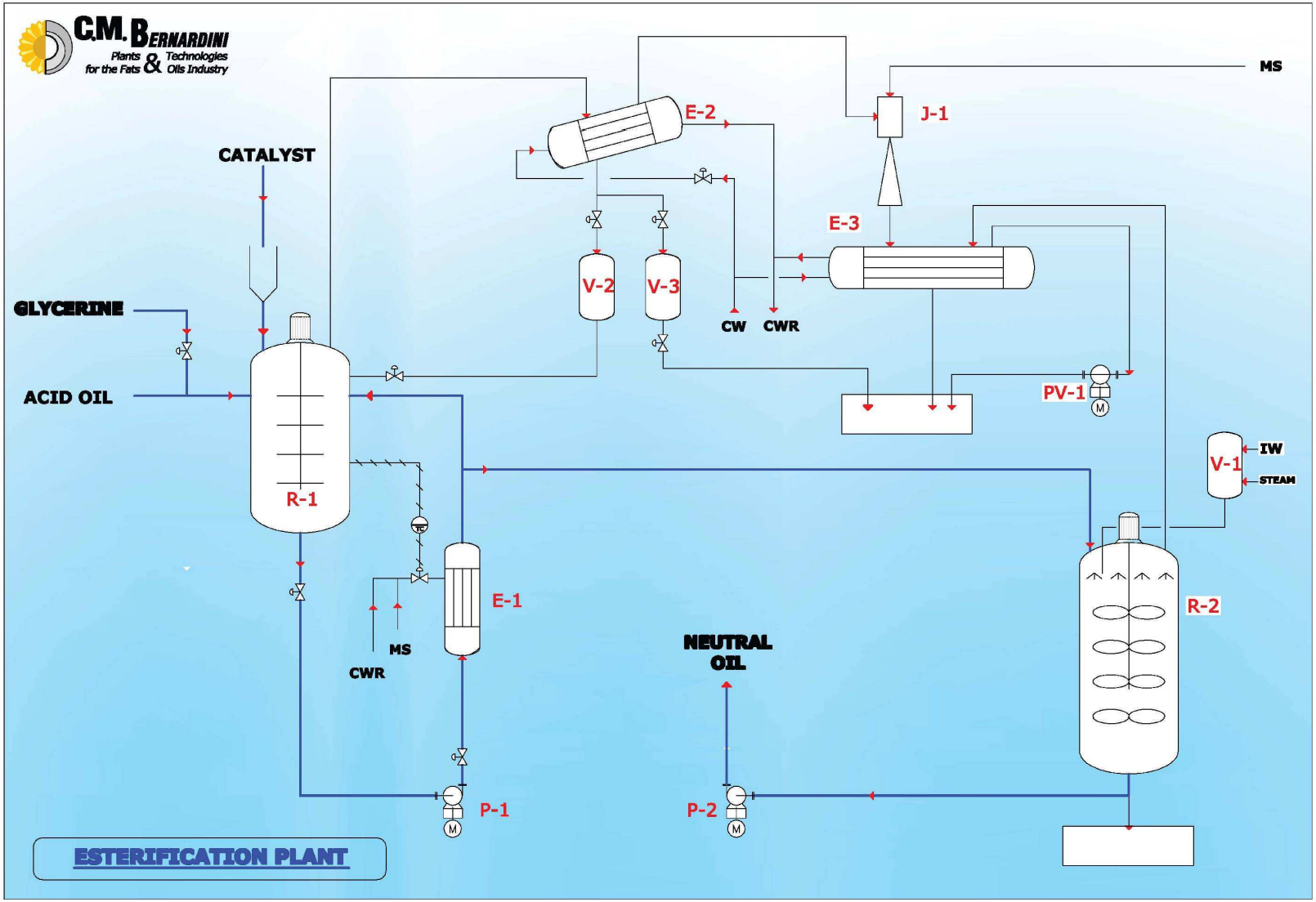
With a proper reaction, it is possible to obtain a neutral oil from high FFA Oil or Fatty Acids with following characteristics:

F.F.A.	0,1 – 0,2%
Moisture	0,1 max

The obtained neutral oil normally cannot be used for edible purposes since there is a formation of mono and diglycerides and also high content of trans fat.

For this reasons normally it is used for industrial application like for example for the biodiesel production.

Many kind of this units have been installed recently by our company for a Biodiesel Unit and paiting industries.



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ESTERIFICATION WITH METHANOL

It is the direct conversion of fatty acids to methylester

Following reaction takes place between fatty acid and methanol.

$$RCOOH + CH_3OH \rightarrow RCOOCH_3 + H_2O$$

Where R is the radical of a Fatty Acid

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ESTERIFICATION CONDITIONS

- Mineral acid catalyst (H2SO4 usually)
- High excess of methanol (typically 10:1 molar)
- Temperature of 80-100 °C
- Pressure of 6-10 bar (to maintain the methanol liquid)
- Not total conversion (due to water formation)
- Sophisticated materials to be used due to the presence of diluted sulphuric acid

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PROBLEMS OF DIRECT ESTERIFICATION

- Esterification with methanol forms dimethylsulphate that is cancerogenuous and cannot be separated by distillation having vapour pressure similar to methylesters.
- Biodiesel from esterification only, exceeds the limit on sulphur content even if distilled
- Sulphuric acid must be neutralised with caustic soda. The resulting sulphates are normally mixed with the glycerine, but precipitates in the distillation fouling the reboiler tubes and requiring very frequent exchanger cleaning

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DIRECT ESTERIFICATION WITH ETEROGENUOUS CATALYST

- Fatty acids can be esterified directly to methylester with eterogenuous catalyst (resins).
- Various commercial products are available, with good results on distilled fatty acids (PFAD or fatty acids from physical refinery).
- There is not sufficient evidence that resins can have a long life on “dirty” materials as soapstock fatty acids.
- Minimum two steps of reaction are required with removal of water+methanol and addition of dry methanol after the first step to achieve a good conversion.

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ACID OIL TREATMENT

Since the soapstock is treated with sulphuric acid, there is the disadvantages to have residual traces of the above mineral acid in the obtained Acid Oil

Therefore, it is very important to remove any traces of sulphuric acid in order to avoid problems of high corrosion during subsequent steps.

Also solid impurities and undesiderable matters have to be removed by further process.

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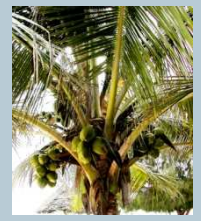

TYPICAL SPECIFICATION OF ACID OIL

SV (Saponification Value), mg KOH/g	**194-204**
Acidity, as FFA % m/m	**50-70**
Moisture, % m/m	**2 max**
Impurities (insoluble in petroleum ether), % m/m	**0,10 max**
Unsaponifiable matter, % m/m	**1,50 max**
IV (Iodine Value), g I2/100 g	**100÷140**
Mineral acidity, % m/m	**absent**
Feeding conditions	**70°C in fully liquid state**

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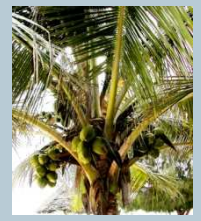
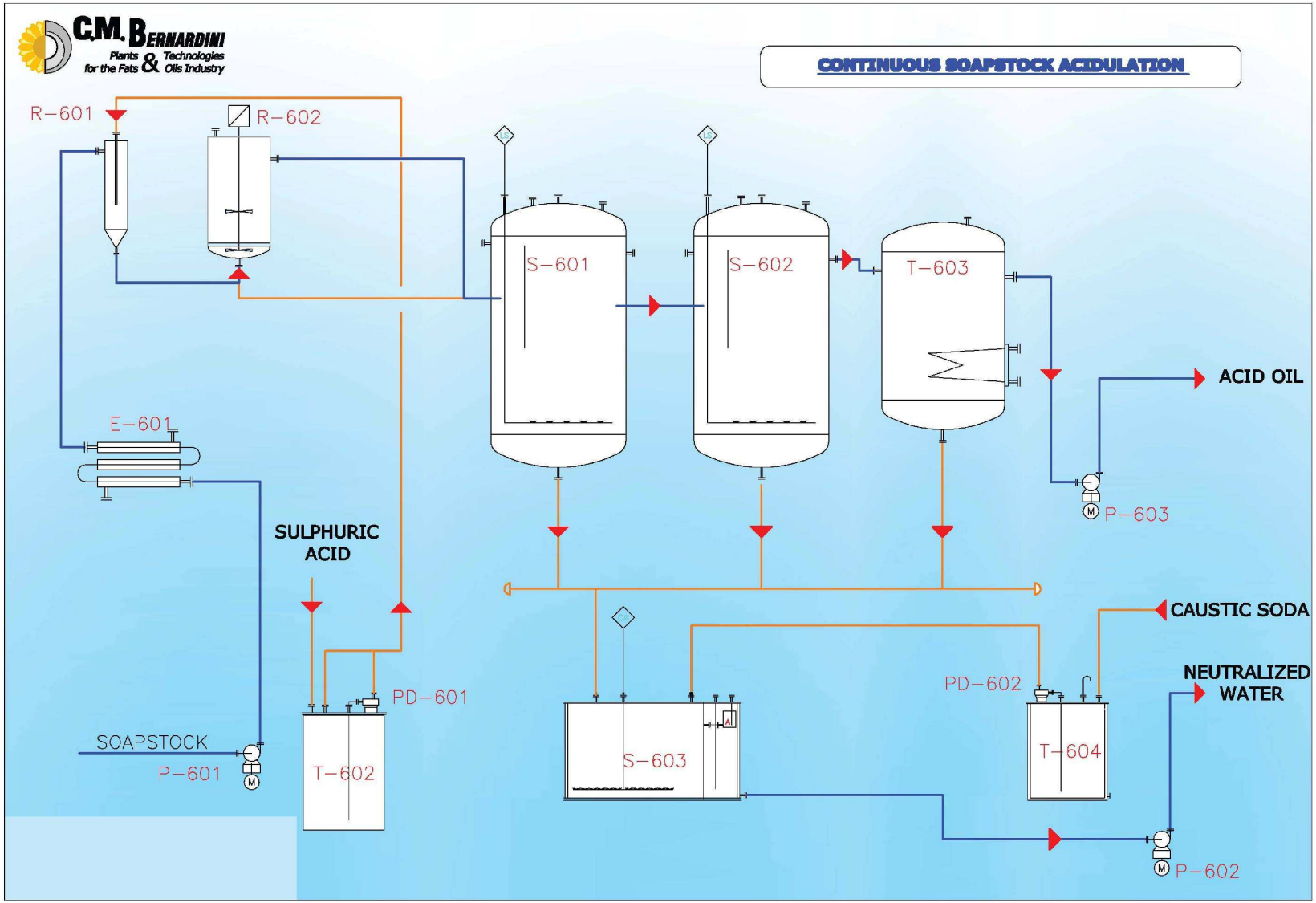


ACID OIL TREATMENT

- **Sulphuric Acid is removed by water washing**

- **Solid impurities are removed by Filtration**



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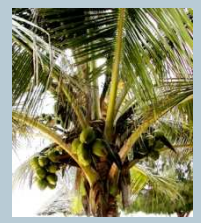


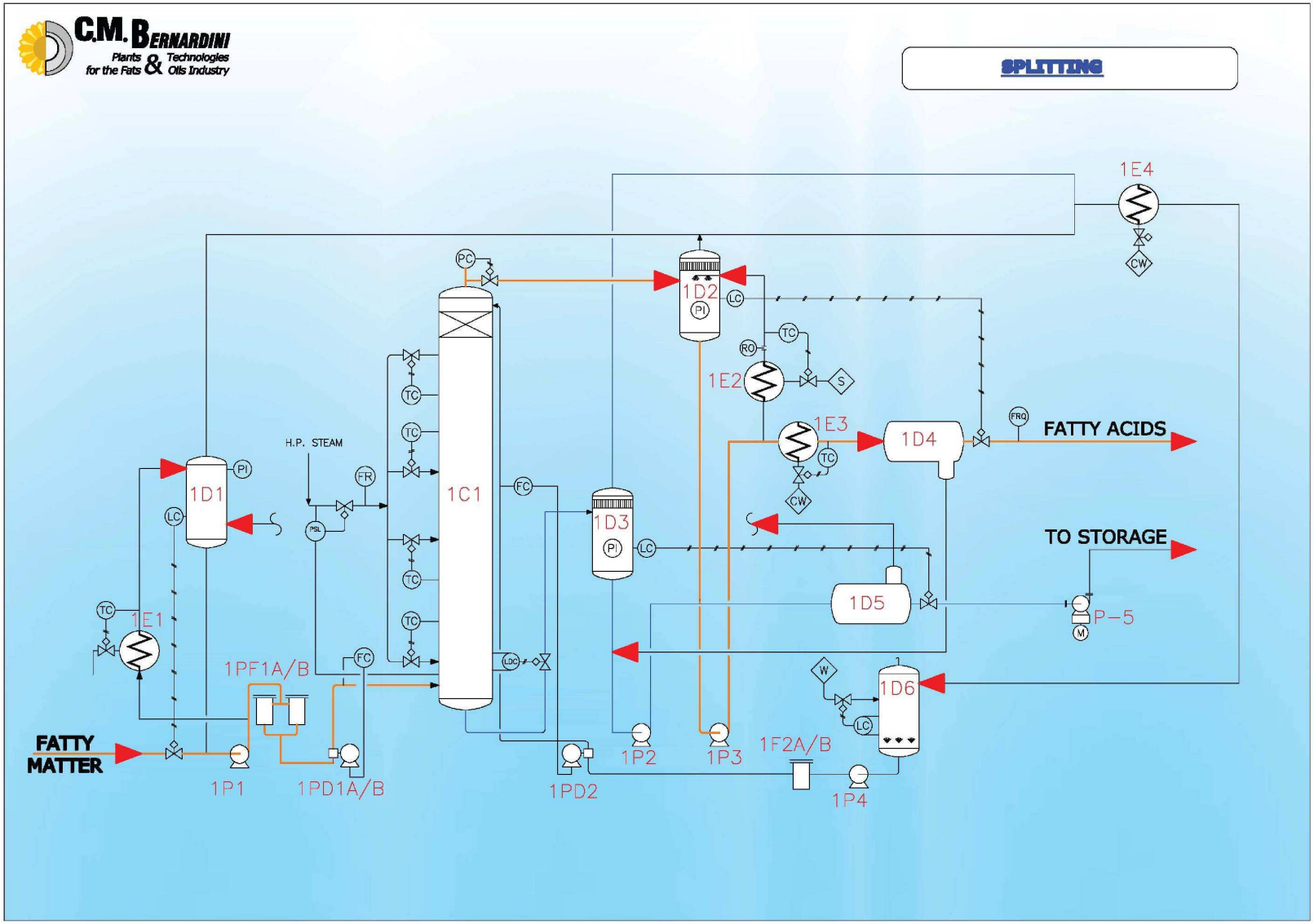
SPLITTING AND DISTILLATION

One of the best use of Acid Oil considered a cheap fat material, is to transform the same in a Fatty Acid to be used in the Oleochemical Industry.

According to the F.F.A. content the Acid Oil can be directly distilled or splitted and then distilled.

Normally with an F.F.A. in the range of 50 – 60%, it is better to split the fat in an autoclave under pressure in order to obtain an high yield of crude fatty acids.

In case the F.F.A. is higher than 70 – 80%, splitting can be avoided and product can be directly distilled.



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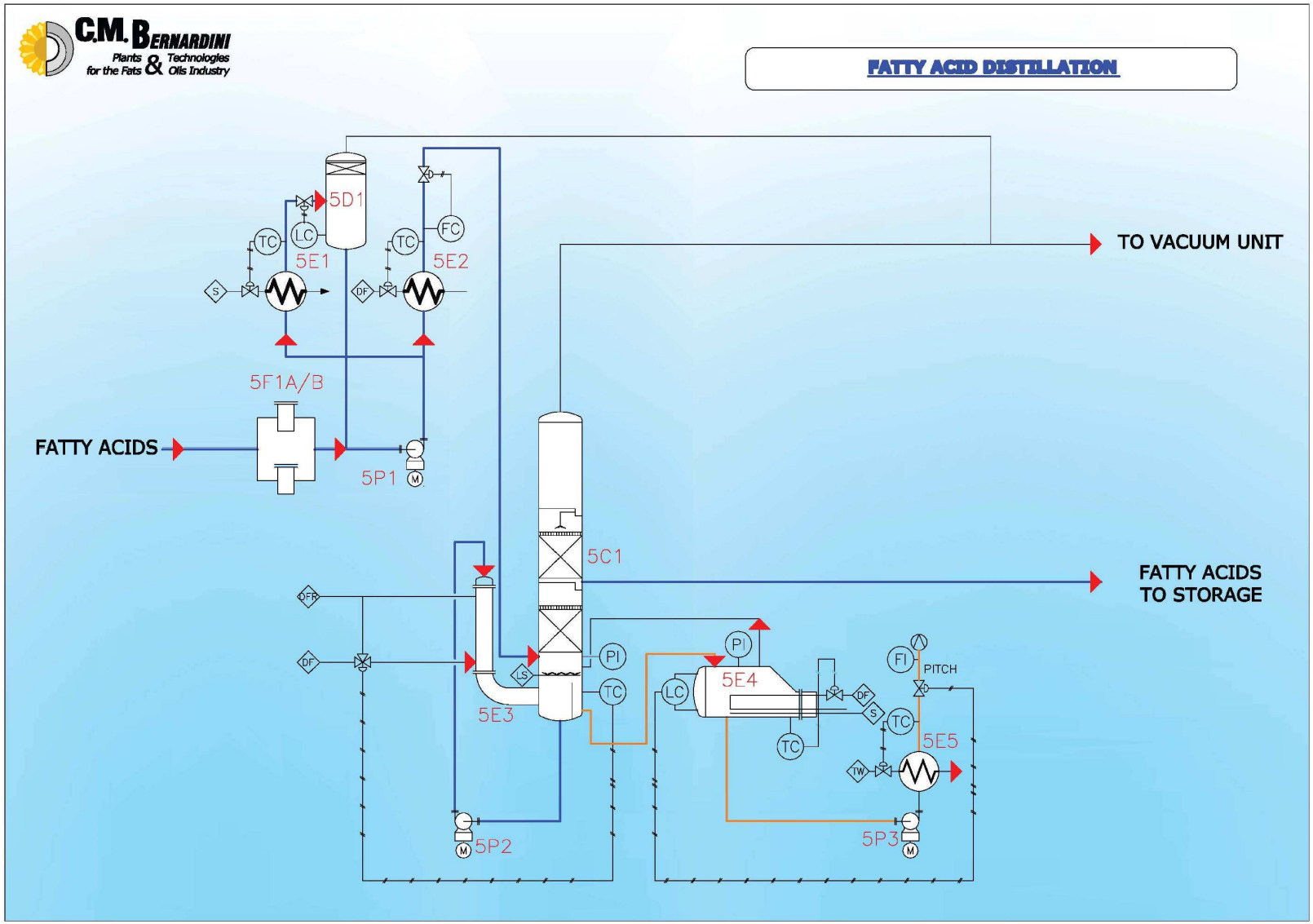

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SPLITTING – DISTILLATION

Advantages and Disadvantages of this route are:

- In case of direct distillation: much more pitches and less yield in Fatty Acid since Fatty Acids from neutral oil are not recovered but, in the other way less investment since splitting unit is avoided.

- With splitting followed by distillation higher yield of Fatty Acids and also better quality of final Fatty Acids since splitting is destroying some of the “bad” components which are present in the Acid Oil. Also glycerine can be recovered.

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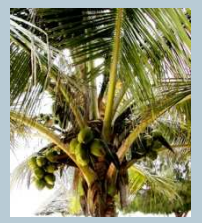

SPLITTING DISTILLATION
How to use the obtained product

- **Fatty Acids from direct distillation:**

Soap industry
Painting industries
Other industrial purposes

- **Fatty Acids from Splitting – Distillation**

Soap industry
Stearic acid
Painting industries

In case a distillation is provided with a precut column (removal of light fraction) a very good quality of fatty acid can be obtained in order to produce toilet soap.

Also Fatty Acids obtained from Acid Oil can be sold to other Oleochemical Industries where are mixed in a relatively small quantity with other high quality Fatty Acids produced from neutral oil.

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TYPICAL SPECIFICATION OF DISTILLED FATTY ACIDS

Vegetable origin

AV	193-203
SV	194-204
IV	100-140
Titer, °C	10-24
Colour, Lov 5 ¼	1-2R; 10-20Y

Animal origin

AV	195-209
SV	196-210
IV	45-60
Titer, °C	38-43
Colour, Lov 5 ¼	1-2R; 10-20Y

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TYPICAL SPECIFICATION OF STEARIC ACID

AV	195-209
SV	196-210
IV	2 max
Titer, °C	55-58
Colour, Lov 5 ¼	0,5-1R; 5-10Y

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OIL RECOVERY
from Bleaching Earth

Composition

Bleaching earth after bleaching: oil content 25 – 30%

Process

Mixing Bleaching Earth with exane with subsequent filtration and solvent recovery, allows to recover all absorbed oil.

The recovered oil can be mixed again with crude oil in order to obtain a full refined oil, provided that the bleaching earth are processed within few days to avoid F.F.A. increasing and further oxidation if stored long time in atmosphere.

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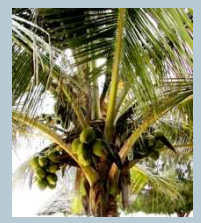

OIL RECOVERY
from waxes - stearine after winterizing.

During winterizing of vegetable oil, in certain case a lot of neutral oil is lost during filtration (due to filter aid and waxes absorption).

Also in this case the neutral oil can be recovered by solvent

Process

A certain quantity of neutral oil, can be recovered mixing “winter filter cake” with hexane with subsequent cooling and filtration. The recovered oil can be mixed again with the crude oil to be processed.

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CONCLUSION

Two important factors have to be considered when such kind of units are installed:

- Quite large availability of raw material (acid oil – bleaching earth – winterization cake) in order to justify the units installed.
- A reasonable price of crude oil that pay back the relevant transformation cost.

In any case, the above alternative process allows the factories to use low quality and low cost material with a great advantages to reduce the waste materials and to obtain in the meantime products with higher add value.

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THANKS

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