IAFMM FISH OIL BULLETIN

international association of fish meal manufacturers

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DISCUSSION DOCUMENT

THE EXTRA EFFORT AND COST TO THE REFINER IN DEALING WITH POORER GRADE QUALITY FISH OIL

1. INTRODUCTION

It is necessary to discuss briefly the quality parameters of fish oil with particular reference to those which affect the usage and "shelf-life" i.e. stability to oxidation, of the hydrogenated edible product. It is high levels of these contaminants which necessitates the use of extra refining treatment, with consequent increase in refining costs. From this discussion definitions arise which have formed the basis of the increased cost calculations.

2. QUALITY PARAMETERS

2.1 "Moisture and Impurities"

The impurities referred to are oil insolubles and consist of rust, proteinaceous material and general dirt. Rust is of importance because iron is one of the principal pro-oxidants of edible oils, and thus leads to reduced stability to oxidation (development of unacceptable flavours). The rust reacts with fatty acids to produce soaps and with other chemicals in the oil to produce co-ordination compounds which, like soaps, are soluble in oil. Iron also affects the final colour of the oil.

The protein contains enzymes which, in the presence of water, increase the free fatty acid content of the oil. It also breaks down to produce chemicals, for example those containing sulphur, which affect the refining, hydrogenation and final quality of the oil.

2.2 Free Fatty Acid (F.F.A)

This is still the best indicator of oil quality in that a high FFA indicates a poor quality oil. Unfortunately, an oil can have a low FFA and still result in a poor edible product, due to oxidation and colour fixation. Increased processing costs arise for these reasons.

For the purpose of the cost comparison the "good" oil has been given a 2% FFA and the poor oil 4%.

2.3 Oxidation Products (Peroxide Value, PV; and Anisidine Value, AV).

The PV and AV must be taken together. Too often, people are misled into thinking an oil is of good quality because it has a low PV whereas, if the anisidine value test is carried out, the oil is shown to be poor.

The oxidation level of the oil must be reduced as far as possible during processing to improve the stability of the end product.

2.4 Ultraviolet Specific Extinction ($E^{1\%}_{1cm}$)

The UV extinction is measured to show the development of conjugation of double bonds in the fatty acid chains. It increases with oxidation but also with processing or storage at high temperatures, and is a good indicator of the reason for colour fixation.

2.5 Trace Metals

Iron and copper, particularly the latter, have a marked effect on oil stability to oxidation. Iron also is linked with colour fixation and deterioration during processing, particularly when there are high levels of sulphur in the oil. Nickel has a similar effect on colour.

2.6 Sulphur and Halogens (Chlorine, Bromine, Iodine)

Much has been written on the effect of sulphur on the hydrogenation of fish oil. For this paper it will suffice to say that trouble can be expected if the sulphur content of the crude oil is over 30 parts per million. With such an oil, extra treatment is needed to reduce the level so far as possible before hydrogenation, but even then more catalyst will be needed than for a good oil.

Less is known about the halogens, except that they are catalyst poisons. Their quantitative analysis is more difficult, as is their removal from the oil.

2.7 Mucilage/Phosphatides

These impurities act as emulsifying agents. High levels are combatted by extra washing and treatment with phosphoric acid and citric acid. They are responsible for the dirt which sticks to the inside wall of the bowl of the soap-stock centrifuge in a continuous refining line. If the plant is not equipped with a self-cleaning bowl, it is necessary to stop the line and clean the bowl from time to time.

The dirt goes with the soapstock and gives further trouble by the formation of emulsion when the soapstock is split with sulphuric acid to produce the acid oil by-product. Extra sulphuric acid and time is needed to split the emulsion, but these have not been included in the costs as they are not significant compared with other costs. The dirt, however, does have a considerable nuisance value in this context.

3. QUALITY DEFINITIONS

The figures in Table 1 are given to illustrate the comments made in Section 2 and to give a clearer picture of what the author considers are good and poor quality oils. The good oil is a good average and the poor would certainly give trouble but is not the worst which has been experienced.

4. PROCESSING

Table 2 compares the processing treatment for the two oils. The purposes of the extra treatments are as follows:

Citric acid wash and extra phosphoric acid - to remove as much mucilage and trace metals as possible.

Extra caustic soda refine - to reduce sulphur and colour.

Heavier bleach - to remove more colour, oxidation products, trace metals and sulphur.

Extra catalyst will be needed in spite of the extra refining treatment given. The actual amount required is difficult to estimate because of the practice of re-using catalyst.

Extra hydrogen has been allowed because more venting of poisons in the autoclave head space is necessary with a poor quality oil.

The extra post-refining and bleaching treatment is necessary to improve colour removal and also because the extra hydrogenation time will probably have put up the FFA to a level which could not be removed satisfactorily in the deodoriser.

The additional citric acid added before deodorising helps to prevent colour deterioration during deodorisation, by chelation of part at least of the trace metals still in the oil.

Extra deodorising time is needed to break down and remove the oxidation products responsible for bad smell and taste. Only batch treatment is shown but the same applies to high temperature semi and fully continuous equipment.

It must be stated that even after the extra refining the quality, in particular the shelf-life of the product from the poor oil, will not be as good as that from the good crude oil.

5. COSTING

5.1 Chemical

Table 3 lists the additional chemical costs and the prices of the individual chemicals used for the calculations.

The additional cost is £13.79 per tonne oil.

5.2 Oil losses

The extra oil losses are set out in Table 4. To evaluate these losses it has been necessary to give a value to the oil at the different stages; these have been estimated from the datum points of crude and deodorised hardened oil prices for the London area in recent (1980) editions of "The Public Ledger".

The additional cost is £11.49 per tonne oil.

5.3 Production Losses

An idea of the extra time resulting from the additional treatment is given in Table 5. Apart from post-refining, the production loss lies between 20 and 25%.

One method of evaluating this production loss is by using the "fixed" and "wage" costs per tonne of oil. These are calculated on the assumption that a certain quantity of oil will be processed in a given time and therefore any slow down in production rate will result in an increase in these costs. The costs vary from refinery to refinery, but a 20% production loss has been calculated to produce an increase in this costing of £12.50 per tonne oil.

6. SUMMARY

Assembling the costs in Section 5, the total additional cost to the refiner is as follows, assuming the parameters stated in the Tables.

Additional cost producing a refined deodorised hydrogenated fish oil melting point 35°C from poor quality oil as against a good oil:

Chemical cost	£13.79 per tonne oil
Oil loss cost	£11.49 per tonne oil
Production loss cost	£12.50 per tonne oil
Total	£37.78 per tonne oil

Associated problems are:-

reduced shelf-life of products,

variation in solid fat index curve, caused by higher levels of catalyst poisons,

variation of product colour (this is particularly important in such uncoloured products as shortenings),

delays in production programme,

extra laboratory analysis time,

extra energy costs.

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TABLE 1

Crude Fish Oil Definitions for Cost Calculations

	Quality	
	Good	Poor
Moisture %	0.1	0.4
Impurities %	0.03	0.1
FFA %	2.0	4.0
Peroxide Value (m.equiv ^{s}/Kg	2.0	9.0
Anisidine Value	5.0	15.0
U.V.Specific Extinction $E^{1\%}_{1\ cm}$ 269nm	1.0	5.0
Iron ppm	1.0	6.0
Copper ppm	0.1	0.5
Sulphur ppm	15.0	60.0

TABLE 2

Processing Stages and Chemicals

Stage	Poor Quality	Good Quality
Neutralising	- Citric acid wash 2% of 10% solution	-
	- Phosphoric acid 0.2%	0.1%
	- 1st refine, 4N NaOH 20% excess (for 4% FFA)	Same(for 2% FFA)
	- 2nd refine, 4N NaOH (for 0.75% FFA)	-
	- 3 washes	Same
	- Dry	Same
Bleaching	- 2% high activity earth	1% standard earth
	- Filter	Same
Hydrogenation	- Catalyst 0.15% as Nickel	0.1%
	- Hydrogen extra 10%	-
Post-refining	- Phosphoric acid 0.05%	-
	- 1N NaOH (for 0.75% FFA)	-
	- 2 washes	-
	- Dry	-
Bleaching	- Citric acid 0.02% as 10% solution	Same
	- 1% high activity earth	0.5% standard earth
Deodorising (Batch)	- 7 hrs at 190°C	5 hrs at 190°C
	- Citric acid 0.02% before deodorising	-
	- Citric acid 0.02% on cooling	Same

TABLE 3

Additional Chemical Costs

Chemical	Cost/tonne oil £
Citric acid	2.20
Phosphoric acid	0.57
Caustic soda (NaOH)	0.61
Bleaching earth	4.16
Catalyst	5.00
Hydrogen	1.00
Sulphuric acid (splitting extra soap)	0.25
TOTAL	£13.79

Costs of Individual Chemicals

	£/tonne
Citric acid monohydrate	1000
Phosphoric acid, S.G. 1.7, Tech.	370
Caustic soda solution 50%	55
Bleaching earth - high activity	206
- standard	135
Catalyst (23% nickel)	2380
Hydrogen	0.141/$metre^3$
Sulphuric acid (77%)	28

TABLE 4

Additional Oil Losses

Stage	Oil Loss (%)	Value Loss(£)	Loss (£)
Citric acid wash	0.3	240 to 115	0.38
1st refine	4.0	240 to 115	5.00
2nd refine	0.5	270 to 115	0.78
1st bleach	0.7	270 to 0	1.89
Post refine	1.0	340 to 115	2.25
Post bleach	0.35	340 to 0	1.19
		TOTAL	£11.49

Approximate Oil Values for Above

Stage	Value/tonne £
Crude oil	240
After 1st refine and after 2nd refine and washing	270
Crude hardened	340
Deodorised hardened	380
Acid oil	115

TABLE 5

Typical Time/Production Losses

Stage	**Method**	**Good Oil**	**Poor Oil**	**% Production loss**
Refine & Bleach	Batch	14 hrs (25 tons)	18 hrs (25 tons)	22
	Continuous	8 tons/hr	6 tons/hr	25
Hydrogenation	Batch	8 hrs (12 tons)	10 hrs (12 tons)	20
Post-refining	Batch	6 hrs (25 tons)	12 hrs (25 tons)	50
Deodorising	Batch	8 hrs (12 tons)	10 hrs (12 tons)	20