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International Association of Fish Meal Manufacturers

1. STANDARD HYDROGENATION TEST FOR FISH OIL

2. PRELIMINARY RESULTS USING STANDARD HYDROGENATION TEST

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1. STANDARD HYDROGENATION TEST FOR FISH OIL

EXECUTIVE SUMMARY

Scientists at the Esbjerg Fiskeindustri, A.m.b.A. in Denmark assisted the Scientific Committee of the Association in developing a method for measuring the rate of hydrogenation of fish oil samples.

Disputes between buyer and seller over the quality of fish oil are often referenced to the speed at which a fish oil can be hydrogenated. A simple hydrogenation test which can be agreed between the buyer and seller might reduce the number of disputes in the future, and could be of use to the seller as a quality assurance test.

With this in mind the reported method was developed by Mr Nils Chr. Jensen working in Esbjerg. The reported method, in section 1, has been edited by Mr F.V.K. Young, the Consultant on Fish Oil to the Association.

In industrial practice the oil is neutralised, washed, dried and bleached to reduce the level of catalyst poisons. It is therefore necessary for reliability and the equating of the test with industrial use that all these refining steps be carried out in a consistent manner before the oil is hydrogenated. The method (excluding the bleaching step in the refining phase) was tested in one laboratory during 1990/91. The results in section 2 indicate that the method is reproducible and can distinguish between good and bad oils. Each test takes one day to perform and it is necessary to conduct tests in duplicate (2 days).

The next step to validate this method should be a ring test of the method undertaken by a number of laboratories using the same samples of oil. The Association decided that this next step should not be undertaken as part of the present programme of work.

1.1 INTRODUCTION

In connection with the working group of analytical methods (Scientific Committee, IAFMM) Esbjerg Fiskeindustri -999- have done some preliminary hydrogenation tests on fish oil. The purpose of the hydrogenation test is to evaluate the hydrogenation ability of fish oil.

This paper describes the method used by -999- in the preliminary test. 'The method is not final and can be adjusted according to the experience that will be gained in any future tests. The paper should therefore be used as a guideline for other laboratories. Later a method can be standardized.

The fish oil has to be refined before it can be hydrogenated. The preliminary tests at -999- have concentrated on the design and handling of the equipment for hydrogenation to find a reproducible procedure. No work has yet been done on optimizing the refining procedure.

The design of the refining equipment is presumably not critical for the test in comparison with the design of the hydrogenation reactor. In a ring test the refining procedure should be standardized, but the design of the equipment could be different from the described.

The hydrogenation reactor was designed in cooperation with Vernon Young (IAFMM Consultant) and it was specially made for this project. The rest of the apparatus with exception of the refining flask are standard equipment.

It is necessary to determine the free fatty acid content in the crude and refined oil, and the iodine value in the refined and hydrogenated oil.

1.2 REFINING

1.2.1 Apparatus

The **refining flask** - see Fig. 1. - is fitted with a heating jacket, which makes it possible to heat the oil indirectly by means of **thermostated water**.

There is a connection to a **vacuum pump** for evacuation and the oil can be blanketed with nitrogen.

A **sprinkler** is built on for addition of phosphoric acid, caustic soda, and water.

The **stirrer** with variable speed control is fitted with blades; the upper set being placed at the same height as the surface of the hot oil.

Stirring can be continuously regulated from 160 rpm to 550 rpm.

The apparatus is used for degumming, neutralisation, washing, bleaching and drying of 1200 g oil.

Commercial availability: The refining flask is not standard equipment but made by Skandinavisk Glasblaeseri Aps, Glentevej 47, DK 2400 København, Denmark (Tel +45 38 33 05 55) at a price of approximately 5000 DKR.

1.2.2 Chemicals

Nitrogen	: N_2-cylinder eg. British Oxygen Co. (BOC) Nitrogen (oxygen-free) SI No 1066
Phosphoric acid	: 50 w/w % H_3PO_4 solution.
Caustic soda	: 2 N NaOH solution with 1 w/w % NaCl. 0.1 N NaOH solution with 1 w/w % NaCl.
Washing water	: 1 w/w % NaCl solution.
Standard Activated Earth	: AOCS, P.O. Box 3489, 1608 Broadmoor Drive, Champaign, Illinois 61826-3489, USA Fax: 217-351-8091

1.2.3 Procedure

Add 1200 g crude fish oil to the refining flask, slow agitation, evacuate the flask - avoid foaming - , release the vacuum with nitrogen and repeat the evacuation twice.[1]

The oil is heated to 65-70°C, stirring with slow agitation.

All chemical solutions (except phosphoric acid) including the washing water are heated to 90°C just before addition.

Degumming.

With fast and turbulent agitation, add 1.8 ml 50 w/w % H_3PO_4 to the oil and wait for two minutes. Then add 100 ml washing water and continue stirring at a gentler speed to give good but not vigorous mixing for further 2 minutes. Stop stirring. Allow the oil to stand until the water has separated, and tap off the aqueous phase.

Neutralisation.

With agitation set for good mixing, 10% in excess of the theoretical amount of a 2 N NaOH solution required for neutralisation of the free fatty acids is dripped slowly through the spray into the oil, and continue the stirring for further 2 minutes. The agitation is stopped. Immediately spray 200 ml washing water (90°C) into the oil, wait until the soap is dissolved, and tap off the aqueous phase.[2]

Washing.

Heat the oil to 85°C before washing. In the washing steps (see below) where stirring is carried out, this is continued for 2 minutes after addition of the washing water. The oil is allowed to stand until the phases have separated, the aqueous phase is tapped off.

1st wash	:	200 ml washing water (90°C) is sprayed in.
2nd wash	:	Slow agitation, 200 ml washing water (90°C) is sprayed in.
3rd wash	:	Slow agitation, 200 ml 0.1 N NaOH solution (90°C) is sprayed in.
4th & 5th wash	:	Slow agitation, 200 ml washing water (90°C) is sprayed in.
6th & 7th wash	:	More rapid agitation, 250 ml water (without NaCl) (90°C) is sprayed in.

[1] The air is replaced with nitrogen to minimize oxidation during the process.

[2] In cases where the soap clumps on the surface, it can be necessary to repeat the last step.

Drying/Bleaching

The oil is dried under vacuum at 90°C with rapid stirring. When the oil is dry the vacuum is released with nitrogen.

1% activated earth is added to the apparatus and the vacuum reapplied. The oil is maintained at 90°C and stirred vigorously for 30 minutes. The oil is cooled to 80° filtered through a vacuum filter.

The oil is now ready for hydrogenation. Preferably the oil should be used immediately. If this is not the case the oil should be stored under nitrogen in the dark in a freezer (ca. -20°C).

1.3 HYDROGENATION

1.3.1 Apparatus

Fume cupboard.

The **hydrogenation reactor** - see fig. 2. - is made of 316 stainless steel.

The reactor is wrapped with a **heating tape** (Electrothermal type HT 95508, 220 V, 244 cm, 400 W plus **power regulator** MC 227).[3]

The temperature in the oil is automatically regulated by **coupling of a pt-100 thermometer** to the power regulator.

To control the temperature a **Hg-thermometer** is also placed in the reactor.

The hydrogen inlet is a **capillary tube** (ID = 3 mm). The end of the tube is bent in a ring with 4 small holes under the ring. The diameter of the small holes is increased from approx. 0.3 mm to 0.5 mm with the largest holes at the end of the inlet tube. You have to test the inlet tube in a glass of water before it is welded to the reactor to be sure that there are outlet from all 4 holes and not only one big hole, and adjust the size of the holes according to the test. The flow is controlled by a **flowmeter** (Porter flowmeter PO F150AV1/RB 125-30/K125SS).

The impeller is a **blade impeller** and the **stirring** can be **regulated exact** from 250-1000 rpm. There are four blades, crossplaced in the blade impeller, each blade is 25 mm from centre to the end and the height is 12 mm. It is a standard impeller, in Denmark it is supplied from several companies like Struers, phone +45 31 70 80 90.

A **10 ml pipette** is placed in the reactor for inlet of nitrogen.

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[3] Heating tape and power regulator are available from Electrothermal Engineering Ltd., 419 Sutton Road, Southend-on-Sea, Essex, SS2 5PH, U.K. (Tel +44 702 612211) at a cost of approx. 800 DKR for regulator and 1000 DKR for tape.

1.3.2 Chemicals

Nickel catalyst	:	G53 with 25% Ni (Sued-Chemie AG, Postfach 202240, 8000 Muenchen 2, Germany. Fax: (089)-511 03 75) should be supplied in small (ca 20 g) sealed sachets and packed, if possible, under nitrogen.
Hydrogen	:	H_2-cylinder.
Nitrogen	:	N_2-cylinder (see section 1.2.2).

1.3.3 Procedure

Place the reactor in a fume cupboard and start the extractor fan. Add 400 g of refined fish oil to the hydrogenation reactor, nitrogen is continuously bubbled through the oil to avoid oxidation during the process, stirring 250 rpm.

Heat the oil to 175°C, switch off heating, add 1.6 g of the catalyst[4] open for hydrogen (flow 1 1/min -), and increase stirring to 1000 rpm, time = 0.

Control that the temperature is between 175°C-185°C during the hydrogenation.

After 60 minutes, stop the hydrogen flow, stop heating, stop stirring, and start cooling the oil e.g. with a fan. After turning off the hydrogen, the nitrogen should be turned on to sweep any remaining hydrogen out of the oil and to help cooling.

The oil is now hydrogenated.

The hydrogenation ability is evaluated by the difference in iodine value before and after hydrogenation divided by the starting IV given as a percentage.

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[4] The amount of catalyst corresponds to 0.1 w%Ni of the oil.

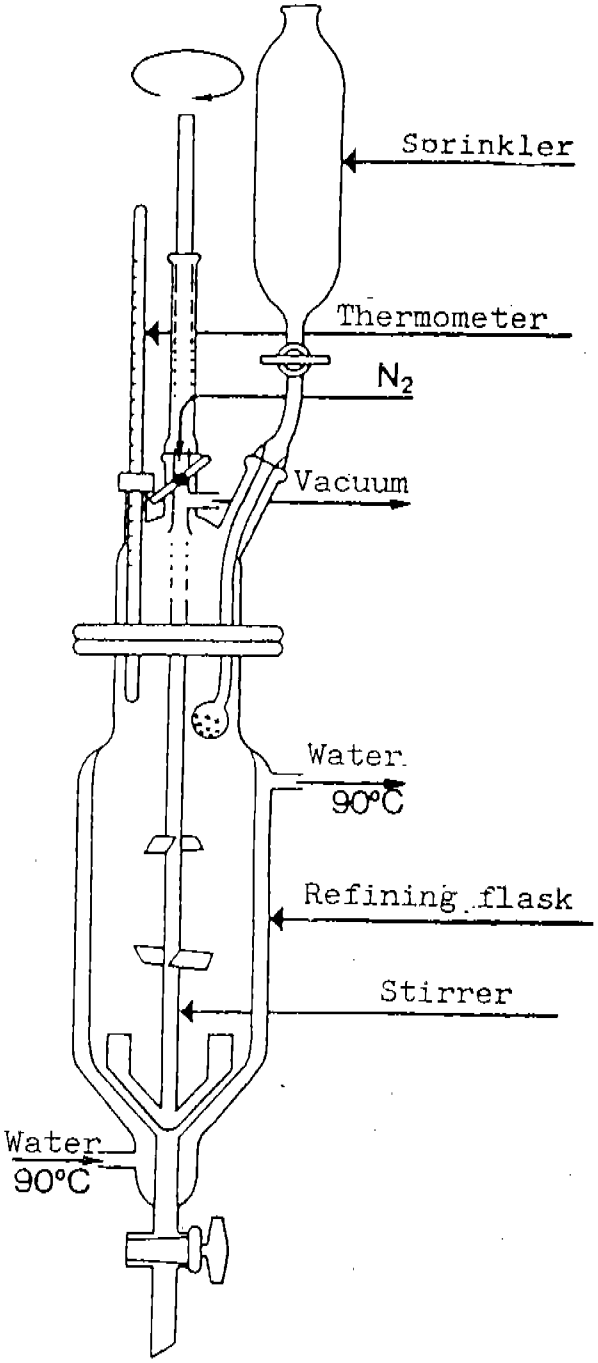

Fig. 1. Refining Flask

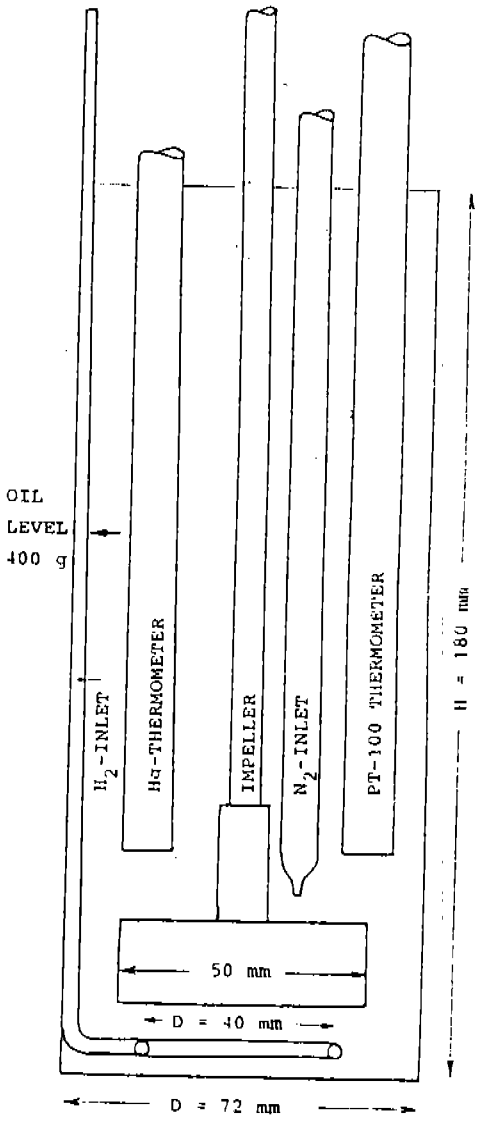

Fig. 2. Hydrogenation Reactor

2. PRELIMINARY RESULTS USING STANDARD HYDROGENATION TEST

2.1 INTRODUCTION

The method outlined in section 1 was tested in the laboratory of the Esbjerg Fiskeindustri, Denmark, during the period 1990/91. Five tests were conducted using fish oils which were easy or difficult to hydrogenate.

2.2 REFINING

1200 g oil is batch refined at 90°C - degumming with phosphoric acid, neutralisation with caustic soda, washing, and drying, but no bleaching.

From each refining there is oil enough for two hydrogenation tests.

2.3 CONDITION DURING HYDROGENATION

Oil : 400 g refined oil

Katalyst : Werk-Girdler G-53. 0.1% Ni added to the oil.

Hydrogen flow : 1 1/min.

Blade impeller speed : 1000 rpm.

Temperature : 180°C (181-177°C).

Time : 60 min.

2.4 RESULTS

2.4.1 Results reported 14.03.90

The first test (2 refinings & 4 hydrogenations).

Oil : refined fish oil with IV = 169.

The oil should be easy to hydrogenate.

Refining no.	IV after hydrogenation A.	IV after hydrogenation B.
I	99.3	98.1
II	99.2	97.7

These results indicate that the test with the modified apparatus is reproducible.

2.4.2 Results reported 28.01.91

The second test (2 refinings & 4 hydrogenations).

Oil : refined fish oil with IV = 151.

The oil should be easy to hydrogenate.

Refining no.	IV after hydrogenation A.	IV after hydrogenation B.
I	94.3	94.1
II	89.2	95.0

The third test (2 refinings & 3 hydrogenations).

The chosen oil (solubles oil) should be difficult to hydrogenate.

Oil : refined fish oil with IV = 150.

Refining no.	IV after hydrogenation A.	IV after hydrogenation B.
I	---	125
II	106	124

The reproducibility is not satisfactory.

2.4.3 New results reported 01.03.91

The fourth test (3 refinings & 6 hydrogenations).

Oil : refined fish oil with IV = 144.

The oil should be easy to hydrogenate.

Refining no.	IV after hydrogenation A.	IV after hydrogenation B.
I	83.2	83.4
II	79.1	76.4
III	* 101	77.5

*Outlier.

The fifth test (2 refinings & 2 hydrogenations).

The chosen oil (solubles oil) should be difficult to hydrogenate.

The ffa content in the crude oil is 16% and due to the loss of oil during refining there is only oil left for one hydrogenation.

Oil : refined fish oil with IV = 142.

Refining no.	IV after hydrogenation A.	IV after hydrogenation B.
I	135	---
II	137	---

2.5 REMARKS

The results indicate that the modified apparatus is reproducible and it is possible to separate a "bad" oil from a "good" oil. It is a sensitive analysis.

One test (fourth) conducted in the laboratory produced an unexplained result which was clarified as an outlier. It emphasises the need to conduct these tests in duplicate. One laboratory technician can refine one batch of oil (sufficient for two hydrogenations) and perform one hydrogenation per day.