

ENERFISH  
Deliverable D8



<b>ENERFISH</b>			
Integrated Renewable Energy Solutions for Seafood Processing Stations			
<i>Project number:</i>	219008	<i>Funding scheme:</i>	Collaborative projects
<i>Start date:</i>	2008.10.01	<i>Duration:</i>	36 months
<i>Call identifier:</i>	FP7-ENERGY-2007-2-TREN		

## Deliverable 8 Raw Material Analysis

Revision	Organization	Date & Visa	Due date of the Deliverable
Written by	TÜV	15.12.2008	
Checked by	All Partners	29.12.2008	
Validated by	VTT	29.12.2008/preliminary version	31.12.2008
Updated by	TUV	22.01.2009	
Validated by	VTT	23.01.2009/updated version	31.01.2009

Project co-funded by the European Commission within the Seventh Framework Programme		
Dissemination Level		
PU	Public	X
PP	Restricted to other programme participants (including the Commission Services)	
RE	Restricted to a group specified by the consortium (including the Commission Services)	
CO	Confidential, only for members of the consortium (including the Commission Services)	

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Deliverable D8

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**DOCUMENT CHANGE LOG**

<b>Revision</b>	<b>Date</b>	<b>Changes description</b>
Draft	15.12.2008	First issue /TUV
Preliminary	29.12.2008	Insertions by Coordinator
Final	31.01.2009	Updated information on further analysis results /TUV

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2	Technische überwachungsverein Rheinland	TÜV	Germany
3	Technofi	Technofi	France
4	National Energy Foundation	NEF	Great Britain
6	Hiep Thanh Seafood Joint Stock Company	HT-FOOD	Vietnam
7	Preseco	Preseco	Finland
8	Vahterus	Vahterus	Finland
9	ECC	ECC	Vietnam
10	RCEE Energy and Environment JSC	RCEE	Vietnam
11	AF Industry JSC	AFI	Vietnam

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## Executive Summary

This document is the contractual deliverable D8 of the ENERFISH project, a project aiming at:

- Develop and demonstrate polygeneration technologies
- Develop and demonstrate a cooling/freezing cascade based on CO<sub>2</sub>
- Realize the demonstration plant in Vietnam
- Demonstrated technology will be exploited and disseminated also in Europe

Fish oil from fish cleaning wastes is used as a source for production of bio-diesel, and electricity and heat at a fish farming and processing plant. Cooling and freezing processes are necessary auxiliary functions at the fish food production, and energy efficient equipments will be also demonstrated.

The deliverable D8 “Raw material analysis” is an output of the Work Package 4 titled “Monitoring and testing plant operation. Analyses (e.g. raw material); Environmental Impact Assessment”. The other WP4 deliverables will be prepared later according to the project schedule.

TUV (Technische Überwachungsverein Rheinland), currently TÜV Rheinland Group, is the leader and main contributor of the WP4. The other beneficiaries of ENERFISH consortium involved in this WP are VTT, HT-FOOD, Preseco, Vahterus, ECC, RCEE and AFI. The early task reported in D8 “Analysis of raw material” aimed to give necessary information on the raw material for the demonstration plant in order to dimension and optimise the demonstration equipments.

The first results of the analyses presented in this D8 will be supplemented by the extensive test results, and the updated report will be published in January, 2009.

## Summary

The materials identified as to be most relevant for the project and process design are the quality of input-water to the process as well as the quality of the fish oil to be processed to bio diesel during the process.

Whilst the water is taken from a local drill at 300 meter depth, that already exists, the fish oil separation plant, processing fish waste to fish oil, is not yet installed.

Both input materials were investigated and subject to analysis. Details about the analysis are presented within this report. The overall findings about existing and proposed qualities of input raw materials are satisfying.



ENERFISH  
Deliverable D8

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## Contents

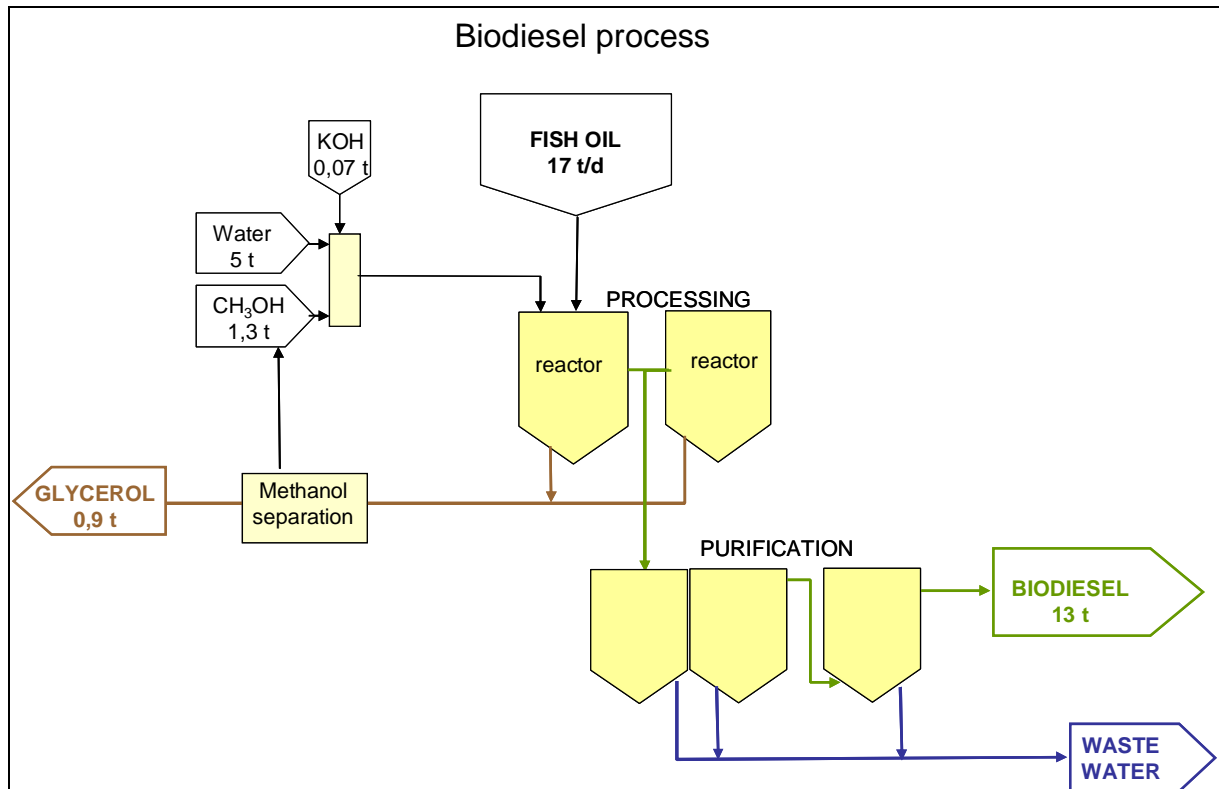
<b>Executive Summary .....</b>	<b>4</b>
<b>Summary .....</b>	<b>5</b>
<b>1 Introduction.....</b>	<b>7</b>
<b>2 Raw materials.....</b>	<b>8</b>
2.1 Analysis of water.....	9
2.2 Analysis of fish oil.....	10
<b>3 Conclusion .....</b>	<b>13</b>
<b>Attachments: .....</b>	<b>14</b>

## 1 Introduction

At the beginning of the project collaborative discussions and bilateral talks helped to get a detailed understanding of the proposed process design and to identify needs for clarifications of raw material analysis. These analyses are intended to support the development and design of the bio diesel plant. The results will be useful as indications on the quality of the raw materials. Anyway, certain safety ranges need to be considered.

## 2 Raw materials

Within the description of works (basis to this Enerfish project) a rough sketch on the proposed process design was already presented.



Source: ENERFISH\_DoW\_final-10\_06\_2008.doc

In total four raw products will be used for the process. In a first premix-tank methanol (CH<sub>3</sub>OH) will be mixed with catalyst (KOH). This premix will be added to fish oil, the third raw material, at a batch reactor tank. Water is also necessary for the process. The main use of water is the purification by which the bio diesel is cleaned before it can be used.

A differentiation of the used raw materials can be done as follows. On the one hand there are raw materials to be used that will be bought and correspond to regular product specifications. The methanol as well as the catalyst is such products. The quality of those products is commonly known and in case any specification will be not fulfilled, the product can be substituted e.g. by selecting of another producer or other product quality.



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Deliverable D8

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Thus, more interesting are these raw materials, that can not be substituted and specifically belong to the selected fish production company.

The input water will be taken from an existing drill at the plant site. Furthermore the fish oil will presumably be taken from the occurring fish waste at the selected site. Currently there even exist three options on how to produce fish oil from fish wastes. By installing a separation plant at the production site, the occurring wastes can directly be processed to fish oil. Second option is to outsource the process of separation by handling fish waste to a service provider and getting back the corresponding fish oil. The third option would be to buy fish oil produced by other fish wastes of another fish factory. Therefore any analysis of fish oil at the current status of the project and only provides preliminary results.

## **2.1 Analysis of water**

The fish production company HT-Food owns a water treatment plant in order to process ground water to drinking water quality. Thus, theoretically two qualities of input water for the bio diesel process exist at the plant. With regard to the intended use of water for premixing and cleaning of bio diesel, the most decisive parameters are the pH and the total hardness. Additionally the water temperature is relevant.

At the water treatment plant in Vietnam several investigations and analyses of water samples have been performed.

The following table summarises the results:

## ENERFISH Deliverable D8

Number	Parameter	unity	Limit / Treshold according to Vietnamese standard for ground water (TCVN5944, 1995)	Result of analysis before ground water treatment	Result of analysis after process
1	pH		6,5 - 8,5	7,62	7,78
2	Color	Pt - Co	5 - 50	0	0
3	hardness as CaCO <sub>3</sub>	mg/l	300 - 500	55,0	50,0 <sup>*)</sup>
4	total solids	mg/l	750 - 1500		
5	arsenic	mg/l	0,05	0,00273	
6	cadmium	mg/l	0,01	below detection limit	
7	chlorine	mg/l	200 - 600	90,04	87,2
8	lead	mg/l	0,05	0,00029	
9	chromium (VI)	mg/l	0,05	below detection limit	
10	cyanides	mg/l	0,01	0,00553	
11	copper	mg/l	1,0	0,00096	
12	fluoride	mg/l	1,0	0,42	
13	zinc	mg/l	5,0	0,0057	
14	manganese	mg/l	0,1 - 0,5	0,01	
15	nitrate	mg/l	45	0,35	
16	phenol compound	mg/l	0,001	0,00027	
17	iron	mg/l	1 - 5	0,68	0,43
18	sulfate	mg/l	200 - 400	62,44	93,8
19	mercury	mg/l	0,001	0,00058	
20	selenium	mg/l	0,01		
21	fecal coli	MPN/100ml	not detectable	0	
22	coliform	MPN/100ml	3	0	

temperature of the water coming from the drill is about 30°C

\*) sum of calcium and magnesium

As it was intended to use the ground water, the water is coming from a 300m deep drill. By this the temperature of the water will presumably be constantly about 30°C both summer and winter times. The pH of the ground water is 7,62. The hardness was determined at 55 mg/l CaCO<sub>3</sub>. As it can be seen by the additional analysis results e.g. microbiological contamination does not exist.

Also analysis results of the water after the process are available. Regarding the crucial parameters (pH and hardness) there are no major changes. As the water treatment is energy and cost consuming process, there is no indication to use processed water instead of ground water.

The option to use processed water due to any unforeseeable reason still exists.

### 2.2 Analysis of fish oil

As mentioned above the final decision on how to provide fish oil / by use of which plant / service provider is not taken yet. Also if there might appear differences in quality of the fish oil depending on its origin can not be finally answered yet. Nevertheless an approach was made by analysis of a fish oil

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Deliverable D8

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sample provided by HT-Food who will also later on be responsible for provision of fish oil.

After discussing with the involved partners, following parameters for fish oil could be of interest:

- Content of free fatty acids,
- density ( $\text{kg/m}^3$ ),
- thermal conductivity ( $\text{W/m K}$ ),
- dynamic viscosity ( $\text{cP}$ ),
- specific heat value ( $\text{J/kg K}$ ),
- moisture content ( $\text{kg/kg}$ ),
- Alkali metals ( $\text{mg/l}$ )
- Sodium ( $\text{mg/l}$ )
- Potassium ( $\text{mg/l}$ )
- Phosphorus ( $\text{mg/l}$ ) and
- Higher heat value ( $\text{kJ/kg}$ ).

Of all these parameters the content of free fatty acids is the most important one, as this is an indication on the quality of fish oil and the possible yield of bio diesel by the process. Furthermore the content of free fatty acids is important for the bio diesel process as it is decisive for the amount of catalyst needed to be added. As more free fatty acids are available, as less catalyst will be needed to start / accelerate the transesterification process. Saving of catalyst is of course also cost-effective.

Parameters like viscosity, specific heat value and thermal conductivity are relevant for the dimensioning of the heat exchangers that will be used for the pre-heating of the fish oil, before the transesterification process is started.

As the bio diesel plant is not yet erected, the determination of free fatty acid content of a nowadays taken sample is only of informative character.

ENERFISH  
Deliverable D8

Also for the dimensioning of the heat exchanger, any results of a current analysis can be used as indication but not as unambiguous, never changing input data. The dimensioning has to be done for a range of values for each parameter.

Nevertheless, the analyses have been performed.

The free fatty acid content was determined by titration test. The result (repeat determination) is 1,5 ml NaOH-solution per ml oil.

The density was determined at 0,92 g/l (at 20°C).

Fish oil samples were analysed at different labs in order to determine the remaining parameters.

As especially thermal conductivity is a very specialized analysis, only few laboratories are in general able to perform this analysis. But meanwhile labs for any parameter have been identified and results were provided. More details about the analyses like applicable standards and testing procedures can be seen in the specific analysis reports in the appendix to this report.

The following table lists all stated parameters and shows the results.

Number	Parameter	unity	Result of analysis	Remark
1	Free fatty acids	ml NaOH-solution per ml oil	1,5	Titration test
2	Density	kg / m <sup>3</sup>	0,92	at 20°C
3a	dynamic viscosity	cP	51	± 0,5 at 40°C, shear rate 50
3b	dynamic viscosity	cP	71,1	± 0,7 at 40°C, shear rate 100
4	thermal conductivity	W / m K	0,173	± 0,003
5	specific heat value	J / g K	2,0 - 2,2	± 5%
6	Moisture content	kg / kg	0,08	
7	Alkali metals	mg / l		
7a	Sodium	mg / kg	< 5	
7b	Potassium	mg / kg	1	± 1
8	Phosphorus	mg / kg	1	± 1
9	higher heat value	kJ / kg	39360	± 46

### **3 Conclusion**

With regard to the short lasting project duration the first feasible and satisfying results were already achieved. All raw materials, as far as necessary, were investigated.

The quality of available ground water is good and will be taken into account for the design of the bio diesel plant.

Regarding the quality of the provided fish oil sample the content of free fatty acids was of main interest. As the result of the titration test showed, the quality of the fish oil is very good.

## Attachments:

- analysis results of ground water
- analysis results of water after process
- analysis results of fish oil (density and free fatty acids)
- analysis results of fish oil (thermal conductivity etc.)
- analysis results of fish oil (dynamic viscosity)

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**Chương V**

**ĐÁNH GIÁ CHẤT LƯỢNG NƯỚC VÀ  
DỰ BÁO BIẾN ĐỔI CHẤT LƯỢNG NƯỚC**

**1- Đánh giá thành phần hóa lý và vi sinh**

Để đánh giá chất lượng nước các giếng khoan của Công ty cổ phần chế biến thủy hải sản Hiệp Thanh, chúng tôi so sánh kết quả phân tích nước lấy tại các lỗ khoan vào cuối đợt bơm nước thí nghiệm với tiêu chuẩn TCVN 5944-1995 (cho phép nồng độ các chất ô nhiễm trong nước ngầm) và được thể hiện trong bảng sau:

STT	Hàm lượng	ĐVT	TCVN 5944-1995	Giếng khoan HT1
1	pH		6,5 – 8,5	7,62
2	Màu	Pt – Co	5 – 50	0
3	Độ cứng	Mg/l	300 – 500	55,00
4	Chất rắn tổng số	Mg/l	750 – 1500	
5	Asen	Mg/l	0,05	0,00273
6	Cadimi	Mg/l	0,01	KPH
7	Cloua	Mg/l	200 – 600	90,04
8	Chi	Mg/l	0,05	0,00029
9	Crom (VI)	Mg/l	0,05	KPH
10	Xianua	Mg/l	0,01	0,00553
11	Đồng	Mg/l	1,0	0,00096
12	Florua	Mg/l	1,0	0,42
13	Kẽm	Mg/l	5,0	0,0057
14	Mangan	Mg/l	0,1 – 0,5	0,01
15	Nitrat	Mg/l	45	0,35
16	Phenola	Mg/l	0,001	0,00027
17	Sắt	Mg/l	1 – 5	0,68
18	Sunfat	Mg/l	200 – 400	62,44
19	Thủy ngân	Mg/l	0,001	0,00058
20	Selen	Mg/l	0,01	
21	Fecal coli	MNP/100ml	Không	0
22	Coliform	MNP/100ml	3	0

So sánh với tiêu chuẩn cho phép theo tiêu chuẩn TCVN 5944-1995, thì nước của giếng khoan khai thác HT1 các chỉ tiêu đều đạt yêu cầu. Tuy nhiên hàng năm cần tiến hành lấy mẫu phân tích định kỳ để theo dõi chất lượng nước so với thời điểm ban đầu.

**2- Đánh giá tác động môi trường**

Trong xu thế phát triển chung của xã hội, ngoài nhu cầu sử dụng nước cho các yêu cầu dân sinh đang không ngừng tăng lên, bên cạnh đó các hoạt động kinh tế

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 Deliverable D8


# Institut Pasteur

**VIỆN PASTEUR THÀNH PHỐ HỒ CHÍ MINH**  
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*Kg. Anh Phan's giao đũa*

## PHIẾU KẾT QUẢ KIỂM NGHIỆM

BM : 01  
 QĐ-LB-PKQ / 00

MÃ SỐ : 30,897 B

Tổng số trang : 1

TÊN KHÁCH HÀNG : ĐOÀN ĐCTV-ĐCCT 804

LOẠI MẪU THỬ NGHIỆM : NƯỚC UỐNG HT 1-ĐG

NGÀY NHẬN MẪU : NGÀY 2 THÁNG 2 NĂM 2007

NGÀY KIỂM NGHIỆM : 02/02/2007

TÌNH TRẠNG MẪU KHI NHẬN : 1CAL NHỰA 2L

## KẾT QUẢ

STT	YÊU CẦU THỬ NGHIỆM	KẾT QUẢ	ĐƠN VỊ	P/P THỬ NGHIỆM	GIỚI HẠN
1	Độ đục (Turbidity)	0	NTU	TCVN 6184 : 1996	< 2
2	Màu (Color)	0	TCU *	TCVN 6185 : 1996	< 15
3	Độ pH	7.78	-	TCVN 6492-2000	6.50 - 8.50
4	Mùi vị (Taste & Odour)	Không mùi vị	-	TCVN 2653 : 1975	Không mùi vị lạ
5	Độ oxy hoá (Chất hữu cơ)	0.16	mg/L	TCVN 6186 : 1996	< 2
6	Amoni (NH <sub>4</sub> <sup>+</sup> )	0.19	mg/L	TCVN 6179-1:1996	< 1.50
7	Nitrit (NO <sub>2</sub> <sup>-</sup> )	0.93	mg/L	TCVN 6178:1996	< 3
8	Nitrat (NO <sub>3</sub> <sup>-</sup> )	Không phát hiện	mg/L	TCVN 6180:1996	< 50
9	Độ cứng (Sum of Calcium & Magnesium) *	50.0	mg/L	TCVN 6224 : 1996	< 300
10	Mangan tổng (Manganese - Mn)	Không phát hiện	mg/L	NF T90-112	< 0.50
11	Sắt (Total Iron - Fe)	0.43	mg/L	TCVN 6177 : 1996	< 0.50
12	Sulfat (SO <sub>4</sub> <sup>-</sup> )	93.8	mg/L	NF T90-040	< 250
13	Clorua (Chloride - Cl <sup>-</sup> ) *	87.2	mg/L	TCVN 6194 : 1996	< 250

GHI CHÚ : Phương pháp thử có (\*) được VILAS công nhận.

Kết quả chỉ có giá trị trên mẫu thử nghiệm - Mẫu thử được lưu 3 ngày sau khi trả kết quả.

### KẾT LUẬN:

Các chỉ tiêu trên nằm trong giới hạn cho phép theo số 1329/2002/QĐ/BYT.

TP. Hồ Chí Minh ngày 9 tháng 2 năm 2007

Phòng kiểm nghiệm Hoá - Lý - Vi sinh  
 VIỆN PASTEUR  
 THÀNH PHỐ HỒ CHÍ MINH  
 PHÒNG KIỂM NGHIỆM  
 HOÁ - LÝ - VI SINH

*KS Phạm Ngọc Liên*

Trưởng Phòng Kiểm Nghiệm



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 Deliverable D8

## TÜV Immissionsschutz und Energiesysteme GmbH

Firma:	Enerfish	Ablieferungsdatum:	
Anlage:	Fischöl	Termin für Ergebnisse:	
Auftrags-Nr.:	21210381	Lagerung bis:	
Position	100	weitere Untersuchungen	
Sachbearbeiter:	Schäfer		

Proben- bezeichnung	Erwartungswerte		Ergebnisse			Proben- gewicht
	abgesaugtes	Konzentration	für die Komponenten			
Einheit	Volumen, l	mg/m <sup>3</sup>	Dichte	freie Säure		g
			g/ml	ml NaOH-Lösung pro ml Öl		
fish oil sample						
Nov 08						
46,13g in 50 ml bei RT			0,92			
viskose Flüssigkeit, die bei 35°C flüssig wird						
doppelten Ansatz genommen, damit die Elektrode in Flüssigkeit steht						
ca. 80 ml von der kräftig gerührten Probe entnommen und auf 45°C erwärmt						
Messung 1				1,5		
Messung 2				1,5		
			sehr gute Qualität			
Analysenverfahren:						gez.:
Analysendatum:						26.11.2008
Sachbearbeiter/in:						S.R.

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 Deliverable D8

# Mikroanalytisches Labor Pascher

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 TÜV Rheinland Immissionsschutz und Energiesysteme GmbH  
 Am Grauen Stein

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Remagen, 05.01.2009

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Ihr Auftrag vom 10.12.2008

*Density*  
*specific heat value*  
*higher heat value*  
*dyn viscosity*  
*thermal conductivity*  
*water content*

Fischöl		
Element	Methode	Ergebnis
Na	AN SOP 1770 AN SOP 1503	< 5 mg/kg
K		1 ± 1 mg/kg
P		1 ± 1 mg/kg
Dichte bei 20,0 °C	DIN 51757, Verf. 4	ca. 0,922 g/cm <sup>3</sup> (siehe Anmerkung 1!)
spez. Wärmekapazität	SOP TA-015	siehe Ergebnistabelle
Brennwert	DIN 51900	39360 J/g ± 46 J/g
dyn. Viskosität bei 20,00 °C ± 0,03 K	DIN EN ISO 3104	nicht durchführbar (siehe Anmerkung 2!)
Wärmeleitfähigkeit	LM STO-014	0,173 W/mK ± 0,003 W/mK
Wasser	DIN 51777	0,08 %

### Anmerkung 1:

Die Probe ist äußerst inhomogen, daher ist hier nur ein Annäherungswert möglich!

### Anmerkung 2:

Bedingt durch die Inhomogenität der Probe verstopft die Kapillare schon zu Beginn der Analyse und die Messung bricht automatisch ab.

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# Mikroanalytisches Labor Pascher

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Seite 2

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## DSC-Messungen zur Bestimmung der Spezifischen Wärmekapazität $c_p$

Kalibrierung mit Saphir, Doppelbestimmung

Während physikalischer Umwandlungen 1. Ordnung (wie z.B. Schmelzen) kann die spezifische Wärme nicht gemessen werden.

Bei der untersuchten Probe treten im unteren Temperaturbereich endotherme Peaks auf. Ein erster Messwert kann daher erst ab 60°C erfolgen.

Probe	Temperatur, °C	$c_p$ , J/g·K
Fischöl	60	2,1 / 2,0
	70	2,1 / 2,1
	80	2,1 / 2,1
	90	2,2 / 2,1
	100	2,2 / 2,2
	110	2,2 / 2,2

Ergebnisunsicherheit :  $\pm 5\%$

Mit freundlichen Grüßen

E.Pascher

## ENERFISH Deliverable D8



ANALYYSIRAPORTTI  
RVT09-002  
22.1.2009

Preseco Oy  
Ilona Kotala  
Tekniikante 14  
02150 Espoo

### VISKOSITEETIN ANALYYSI

Analyysissä käytettiin Brookfieldin Dial Reading Viscometer mallia RVT. Instrumentti kiertää tuntoelintä(spindel) nesteessä ja mittaa tarvittavan vääntömomentin jota tarvitaan ylittämään aiheutetun liikkeen viskoosisen resistanssin. Mitattu %-vääntömomentti on suhteessa mitattavan nesteen viskositeettiin.

**Kaikki mittaukset on laskettu käyttäen "the Brookfield Factor Finder" korttia käännettäessä vääntömomenttilukemaa yksikköön centipoise (cP).**

Näytteet ovat sekoituksia eri komponenteista ilmoitetuissa suhteissa. Näyteastianä käytettiin 600 ml dekanterilasia, Näytettä "Mekong" mitattiin noin 850ml, 1000ml dekanterilasiin. Ennen lukeman kirjaamista lukemakiekkoo sai pyöriä vähintään 5 kertaa.

Mekong	°C (± 0.1)	Spindel	Shear rate (leikkaus nopeus)	Centipoise (cP) / (mPa*s)
	40	1	50	51 (± 0.5)
	40		100	71.1 (± 0.7)

Kunnioitavasti

Minna Lundberg,  
Yrkeshögskolan Novia