ENERFISH

Integrated Renewable Energy Solutions for Seafood Processing Stations

Project number:	219008	*Funding scheme:*	Collaborative projects
Start date:	2008.10.01	*Duration:*	36 months
Call identifier:	FP7-ENERGY-2007-2-TREN		

Deliverable 2

By-products, additives and waste management in the integrated energy poly-generation plant at fish production station

Revision	Organization	Date & Visa	Due date of the Deliverable
Written by	Mona Arnold, VTT	30.4.2009	
Checked by	All Partners		
Validated by	VTT		

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)	

DOCUMENT CHANGE LOG

Revision	Date	Changes description
Draft	30.4.2008	First issue
Final	31.12.2008	

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Summary

The report describes the process of producing fish oil biodiesel from fish waste and the management of by-products and waste streams generated in the process. The case study is HiepThanh Seafood company (HT Food) in Vietnam, producing14 t/day pangasius filets.

Starting from an input of 77 t/d fish waste the process will produce 13 t/d biodiesel. The by-products are ca 15 t/d fish protein waste (from the oil separation unit) and 3.5 tn/d glycerol. Furthermore, the biodiesel plant generates 35 m³/d waste water (soap water) and the optional oil separation ca 50 m³/d waste water.

The fish protein fraction can be utilised as animal feed, biogas substrate or it can be composted. The best economical benefits are achieved by using it as animal feed for a number of different livestock, of which there are worldwide references.

Proven low cost feasible concepts for the utilisation of small scale generation of glycerine are direct incineration combine energy utilisation. This requires desalting of the crude glycerine. Cofermenting the crude glycerol with waste water sludge, biodiesel soap water and other locally available organic waste streams combines both glycerol utilisation and local waste management to produce local fuel (biogas). No pretreatmeant of glycerol is required. Crude glycerol can also be used as a feed additive. This requires analysis and control of the crude glycerol, especially with regard to its methanol content, is necessary.

Purification to high grade glycerol (99.7 %) is economically feasible only in large scale production. In Europe, investment in refinery considered economical for glycerine generation> 25 t/d. 95 % of all current glycerol applications use refined glycerine. Refining and marketing of additional products adds complexity and cost, but also can increase potential revenue.

The waste water generated in the biodiesel process can in the first place be treated in the existing waste water treatment facilities of the fishery. Concentrated waste water flows are also potential cosubstrates in biogasification.

One challenge with fish oil biodiesel its low oxidative stability leading to the formation of insoluble gums, which may cause severe damage in equipment utilizing the fuel. Addition of an antioxidant is essential. Depending on the dosage needed, the cost of antioxidant in Europe lies between 1 and 6 c/l biodiesel. However, the amount of active ingredient as well as the efficiency of product on a certain biodiesel grade varies greatly making the comparison of prices complicated.

Contents

1 Introduction

The report is the Deliverable D2 "Solutions for waste management and biofuel and compost production for the integrated plant" of the project Work Package 2 "Detailed development work for the individual subsystems of the integrated energy system". The background of the task lies in the optimising the usage and create added value of all sidestreams generated in biodiesel production, based on fish oil, taking into account both European and Vietnamese markets. Worldwide, the conversion of waste material to fuel can bring a sustainable economical advantage for the fish industry, besides solving problems with the discharge of the waste.

The report is concerns the management of by-products, additives, wastes and waste water of the integrated biodiesel production process at HT Food *Pangasius*-fish production site in Vietnam. An overview of the production plant mass flows is given in figure 1.

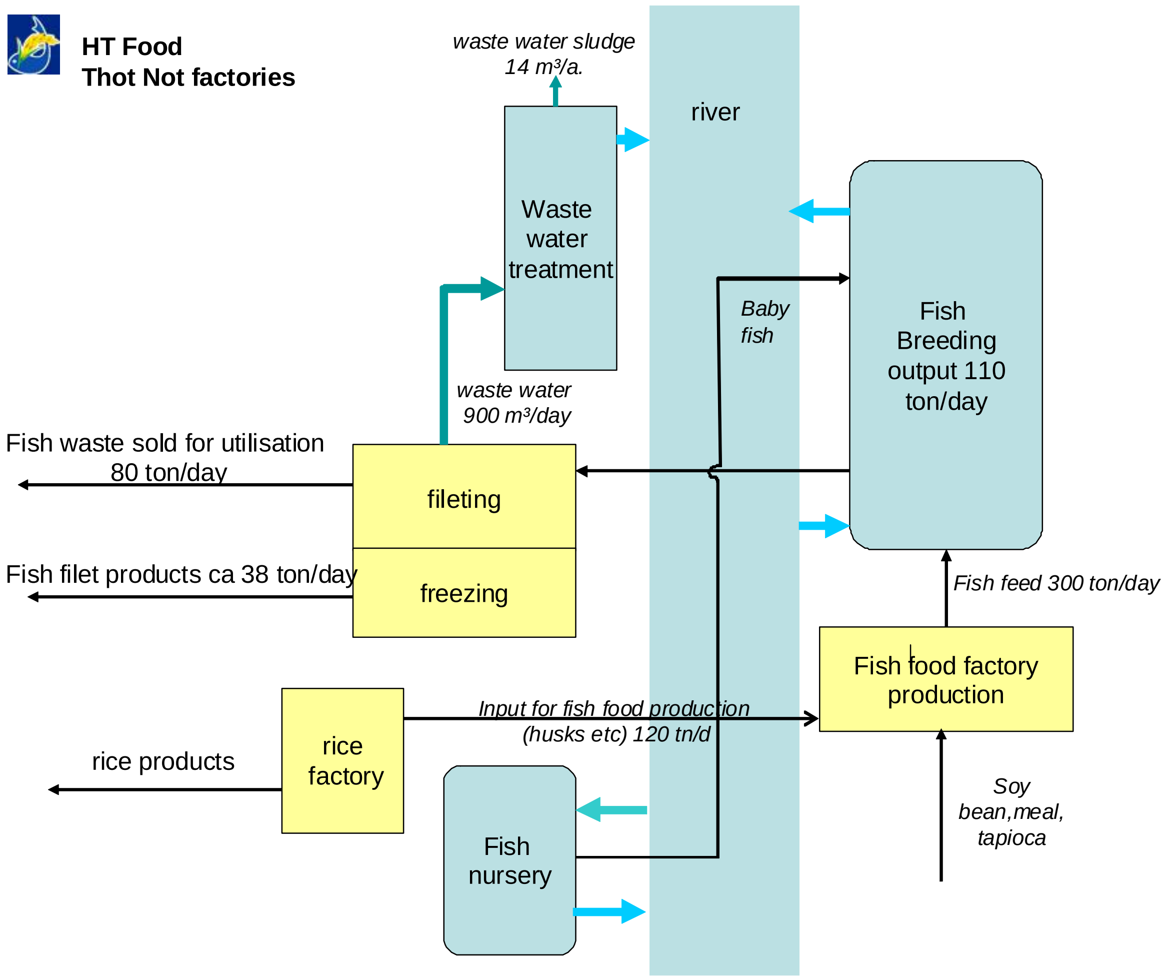

Figure 1. Fish production at HT Food in Thot Not, Vietnam.

The plant produces ca 80 ton /day Pangasius wastes, consisting mainly of bones and offals. As fish oil is the starting material in biodiesel production, the overall biodiesel process includes the option of on-site preparation the fish oil from the fish wastes generated. For the time being, the waste is sold to a third party.

Worldwide some 600 000 tons of fish oil is produced as a commercial commodity. The major producers are Peru, Chile Denmark Norway and Iceland. Lately fish oil production is decreasing, in line with declining fishmeal production worldwide. One reason is the competition with rapeseed oil as rapeseed prices has started to fall (Josupeit 2009). The falling demand for fish oil calls for new utilisation concepts, one of which can be biodiesel production.

This report was written during the first part of 2009 and is based on the market situation at the end of 2008.

2 General description of production of biodiesel from fish waste

The process involves the preparation of fish silage from fileting wastes, fish oil separation from the silage, and the actual biodiesel process. The following chapters give an overview of the process stages. The side-streams are calculated using the Finland based company Preseco Ltd process' mass flows as a basis.

2.1 Silage production of fish cleaning wastes

Fish silage is a liquid product produced from fish waste, to which acids are added, with the liquefaction of the mass provoked by the action of enzymes from the fish (FAO, 2003). It is a common way to preserve and transform fish waste into a product for oil and animal feed ingredient production. Silage is an easy-to-make product which requires low investments (de Arruda et al. 2007). Silage production of the fish waste involves the preservation by adding an acidic agent to the collected waste. The method is easy and does not involve any expensive equipment.

Several acids can be used, either alone or in combination. Hydrochloric or sulphuric acid are reasonably cheap, but a lower pH is required with these mineral acids than with some organic ones, and this means greater corrosion problems, and the silage has to be neutralized before use. Formic acid, an organic acid, is a good choice because preservation is achieved at a slightly higher pH, it has some bacteriostatic action, and the silage need not be neutralized before adding it to the feed, but it is more expensive than mineral acids (Tatterson and Windsor 2001).

Fish processing waste from the production line is fed to a crusher/homogenizer-unit. The waste is crushed and simultaneously formic acid (2.5% w/v) is dozed into the suspension to lower the pH < 4. This homogenous acidified suspension (silage) can been stored for months. Inside the storage tank the silage will naturally start to separate into three faces; the water phase sinks to the bottom, the protein fraction in the middle and the oily fraction stays on the surface. Pre-treatment of the fish waste should be performed as soon as waste is been formed to ensure high quality oil production and also increase the oil yield. If not processed immediately, the fish waste degrades rapidly and quickly looses its value.

2.2 Waste fish oil separation

Various processes are known for the manufacture of fish oil. Those more or less complex processes, depending on the countries concerned, generally consist in cooking the raw material (that is, the fish waste) and then in transferring the cooked product into a decanter in order to remove the water; the water is treated in order to recover oils, and the solid material is introduced into a press which separates the liquid and the solid materials. The solid materials are dried and used, for example, in animal feed and the water led to waste water treatment.

Modern processes for recovering oils and raw fats are characterized by the broad application of centrifugal clarifying and separating technology. The quality of the end product depends on the production process as well as on the nature of raw materials and products used.

In Preseco's process the silage is heated up to 90 °C, pumped to settling tanks and left to settle. During the settlement the suspension is divided by gravitation into three fractions: oil as lightest phase on top, the water fraction, having the highest density, sinks to the bottom. In between these layers is the protein fraction, that can be utilised e.g. as an animal feed ingredient.

The purpose of the heating process is to liberate the oil from the fat depots of the fish, and to condition the material for the subsequent treatment. The heating procedure also works as a hygienisation process according to the EU regulation (70°C for 20 min). After settling, the oil is pumped to intermediate storage, the water fraction is removed from the system and the remaining pulp runs through a tree-phase decanter which separates solid particles from liquids and also the liquid phase into oil and water.

The oil phase from the decanter contains still small quantities of free water and solids. The oil can be polished in a separator or let for passive separation in a settling tank from which solid residues can be collected from the bottom

The overall mass balance of the fish oil separation waste corresponding to a fish production of 110 t /d is given in Figure 2.

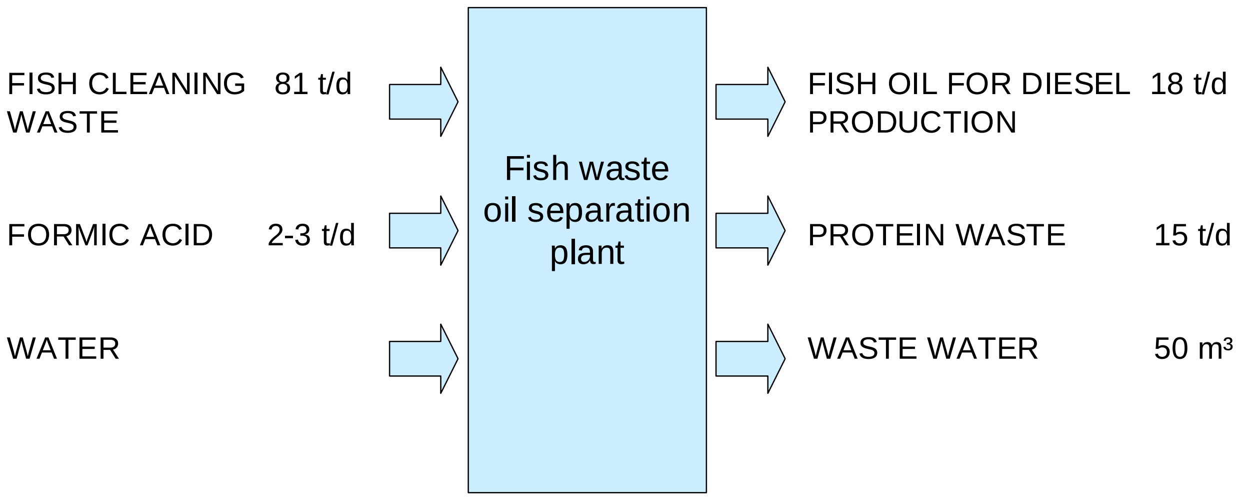

Figure 2. Fish oil separation

The oil separation plant described above is optionally included to be integrated into the overall project. Alternatively the oil is separated at as existing, external site.

To be completed with information about existing local technology (not available at the time of reporting).

2.3 *Biodiesel production*

Biodiesel is made by converting natural oils into fatty acid methyl esters (FAMEs), in a transterification process. This simple process reacts the raw oil with alcohol, usually methanol, in the presence of a catalyst such as sodium hydroxide. As follows, the process provided by Preseco Ltd is described.

2.3.1 Transterification

Biodiesel is produced in batches of 2 m^3 raw material oil. The raw material is stirred and heated to ca 55 °C. Then the solid catalyst is added to a premixer where it is solved into 0.4 m^3 of methanol and fed into the reaction tank. The required catalyst amount is defined by titration test.

The mixture of oil and premix will be mixed and circulated for approx. 1½ hours during which methyl ester (biodiesel) is been formed in a reaction called trans-esterification.

After reaction period the whole batch is pumped into a settling tank for glycerol settle to bottom of the tank by gravity (glycerol has higher density compared to biodiesel). The glycerol is then transferred to a separate glycerol tank from where the methanol residue is distilled and redirected for re-usage. The distillation of methanol continues several hours, after which glycerol is removed from the process to intermediate storage. After methanol removal and cooling the glycerol will transform into a thick solid mass.

2.3.2 Washing

The crude biodiesel undergoes two washing processes. The first washing, done by sprinkling with hot water, removes the catalyst generating very alkaline soap water (pH ~13). The first wash water wash also contains some residues of the biodiesel. Remaining residues of the catalyst is removed in a similar second wash. Here the water wash is boosted with feeding pressurized air to the washing tank simultaneously with water inlet. The pH of the waste water from the second wash is close to neutral and drained from the system.

The washed biodiesel is centrifuged to remove water residues and antioxidants are added. The product is still polished by salts to remove possible moisture still left in biodiesel. Biodiesel is then ready to be pumped out of the system to a storage tank.

The overall mass balance of the process corresponding to a fish oil input of 18 t/d is given in Figure 3.

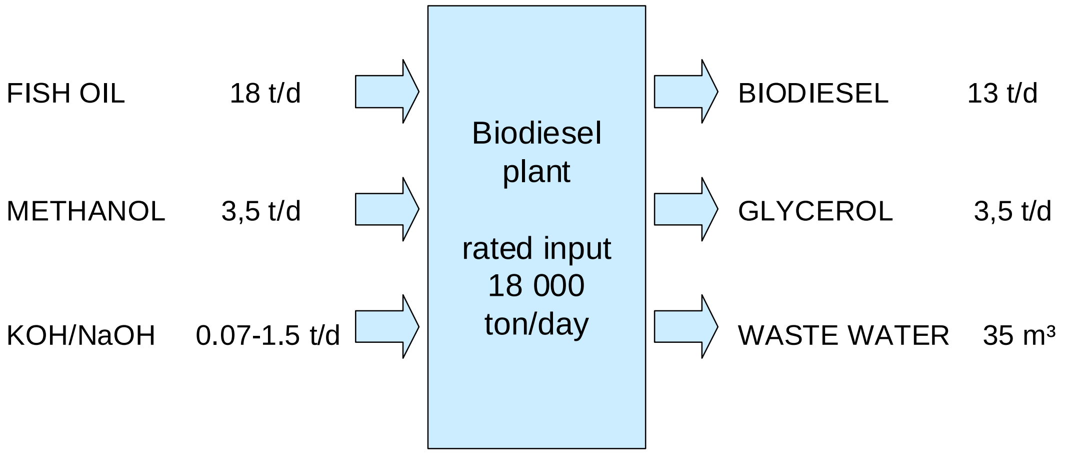

Figure 3. Biodiesel production process.

3 By-products

The main by-products obtained in the overall process are protein waste from the optional oil separation unit and glycerol from biodiesel production. Both by-products have a potential economic value.

3.1 Protein fraction

Some 15 t/d of protein is formed in the oil separation unit, which is optionally planned to be included in the process. Physically the protein fraction is a loose paste that can be pumped and transported in tanks.

The protein fraction from the oil separation is has a good nutritive quality and can, therefore, be very useful in animal feeding (de Arruda, 2007). As for the amino acid content, lysine, threonine and sulphur containing amino acids are present in high levels. Consequently, fish silage would appear to be an excellent protein supplement for non-conventional livestock feeding systems (Tatterson and Windsor 2001).

According to research one very suitable outlet for the silage protein is in pig farming, since it can be used in liquid feeding systems. The fraction can be used alone, or as an ingredient in a mixed feed. Some feeding trials have shown that pigs grow as fast on silage as on e.g. fish meal, and the quality and flavour of the meat is good. Fish silage is used in the Danish pig industry, and most nutritional work has been done there. Other animals have been fed on silage with good results; e.g. duck, cows and chicken. The feed has not affected the taste or odour of eg. milk and butter or egg (Tatterson and Windsor 2001).

In Europe fish offal silage is classified as Category 3 animal by-product. This low risk animal by-product can be processed in a processing plant, transformed in a technical plant or used as raw material in a petfood plant. It may also be transformed in a biogas or composting plant. The use as feed for ruminants has been restricted in Europe.

When used as feed the regulation (EC) No 183/2005 lays down requirements for feed hygiene including e.g. arrangements for registration and approval of establishments.

3.2 Glycerine

The transesterification process giving 13 t/d biodiesel, will produce as a by-product 3.5 t/d. This crude glycerine contains methanol residues, salts and organic residues. In principle, a very wide range of different utilisation concepts is possible (Figure 4). In practice utilisation depends on glycerol market situation.

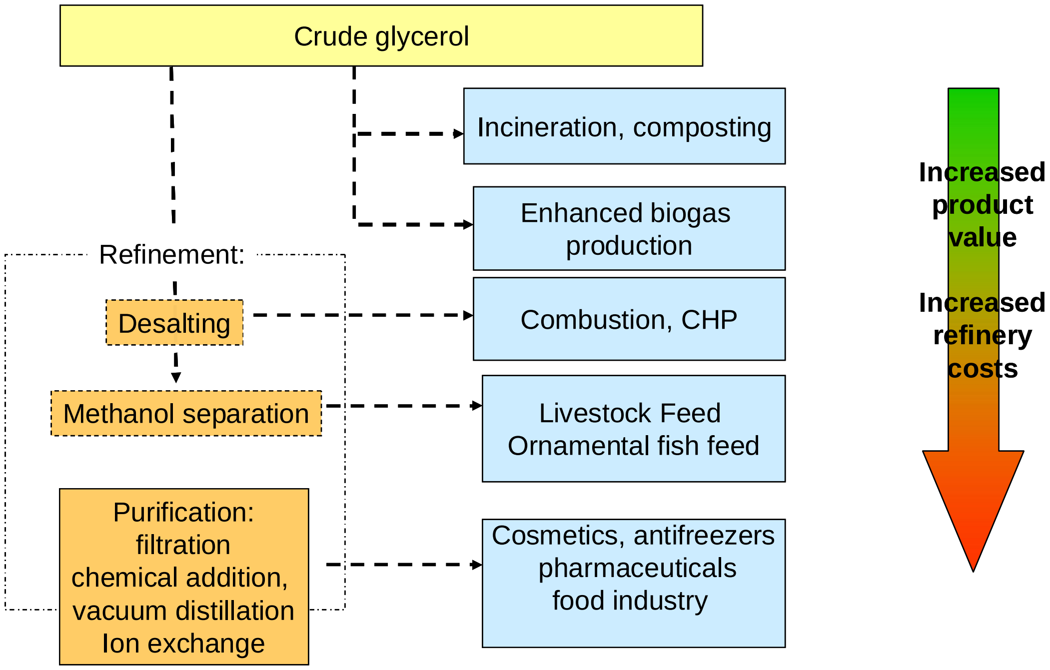

Figure 4. Utilisation of glycerol generated as a by-product in biodiesel production.

An overview of different utilisation options and their economic feasibility is given in appendix 1.

4 Additives

4.1 Formic Acid

Formic acid is used for the production of fish silage for oil separation. In preparation the choice of preservation reagents is made from inorganic acid, a mixture of acids, organic acids or the mixture of organic and inorganic acids. Organic acids, such as formic acid, are generally more expressive than the mineral ones. However, they produce less acid silages that do not need to be neutralized before being used.

Formic acid are generally more expensive than common inorganic acids, but produce silages that are not excessively acid, and, therefore, do not need neutralization before being used (de Arruda et al. 2007). Using formic acid the mass is hydrolysed to a stable product at a pH of 4. If mineral acids are used, the acidity must be reduced to pH 2 for stability (FAO 1986).

Given that the formic acid addition is 2.5 %, the overall consumption of formic acid is ca 450 kg/d. The cost of chemical in Vietnam was not available at the time of writing

4.2 Catalyst

Both caustic soda (NAOH) and potassium hydroxide (KOH) can be used as a catalyst in biodiesel production. NaOH is more commonly used because of its lower price. Potassium salts are less hygroscopic, that is they absorb less water from the atmosphere, so are less likely to cake. Another advantage of KOH is that it dissolves more readily in methanol compared to NaOH and thus it is more reactive. Some biodiesel producers have reported that by using KOH, the glycerine stays in liquid form and is thereby easier to drain and remove from the process. In case the biodiesel wastes or residues are composted, potassium salts are less harmful to the soil than NaOH, and this facilitates the use of compost.

KOH is preferable when the starting material is of low quality and the content of free fatty acid (FFA) is very high.

Again, the main advantage of NaOH over KOH is that both the cost of chemical and the consumption is smaller.

To be completed with local price data on KOH and NaOH.

4.3 Methanol

The biodiesel production process will consume 3.5 t/d methanol.

To be completed with local information on price and availability.

4.4 Antioxidants

The addition of antioxidant to the biodiesel is essential in order to avoid the formation of degradation products, such as insoluble gums and sediments, or the formation of organic acids and aldehydes that may cause engine and injection problems. To retard oxidative degradation and to guarantee a specific stability, it will be necessary to find appropriate additives for the fish oil derived biodiesel. Appendix 2 gives a review of the use of antioxidants for biodiesel processed from fish oil biodiesel. *Local information on price and availability was not available at the time of reporting.*

5 Waste water treatment

5.1 Waste water

The process will produce 50 m³/day waste water from the oil separation unit and 35 m³/d soap-water from the biodiesel plant.

Wastewater from biodiesel production has a high pH and high content of organic carbon (oils) and low nitrogen concentrations. The biological treatment of soap water *per se* is difficult because the composition of such wastewater is not suitable for microbial growth. Some research indicates inhibition of the growth of microorganisms (Sueharta et al 2005), which is probably due to the presence of long chain fatty acids (LCFA) (Gumisiriza et al. 2009). The waste water flow should be diluted into another waste water flow. Enhanced oil or lipid degradation has been reported for diluted soap-waters, especially after an external nitrogen source has been introduced to the soap water (Sueharta et al. 2005). Here the waste water from oil separation, which has a high concentrations of protein (and lipids) is a good completion. To overcome the problem of low bioavailablity of lipids and oils, the separation of solids from the waste water before leading it to biological treatment, is essential e.g. by flotation. For disposal of the resultant flotation sludge both composting and biogasification is suitable.

To be completed with analyses results on waste water and soap water from fish oil separation and biodiesel plant. This information was not available at the time of reporting.

5.2 Integration into existing waste water treatment facilities

The existing waste water treatment plant at HT Food has a capacity of 900 m³/d (Figure 5). In 2007 some 320 000 m³ was pumped. The waste water is aerated with compressed air, and floating and sinking particles are separated before the water is lead to the Mekong river. The amount of sludge produced is very small, only 16 m³/a.

The waste water generated, 35 (biodiesel process) + 50 (oil separation) m³/d can be led into the existing waste water treatment facilities.

An alternative way of treating waste waters from the fishing industry is biogasification. This waste water is, as a rule, heavily contaminated with organic material. The waste water fractions (including contain both lipids and proteins) have high methane yield potential (Gumisiriza et al. 2009). Thus the waste water generated are potential cosubstrates for biogas production.

Figure 5. Waste water treatment facilities at HT Food.

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

Deliverable 2
Utilisation of Glycerine

Revision	Organization	Date & Visa	Due date of the Deliverable
Written by	VTT Mona Arnold		
Checked by			
Validated by	VTT		

Project co-funded by the European Commission within the Seventh Framework Programme		
Dissemination Level		
PU	Public	X
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Contents

1 Introduction

Glycerine is the main by-product obtained when making biodiesel. For every 9 kg of biodiesel produced, about 1 kg of a crude glycerol by-product is formed. The usage of low-grade quality of glycerol obtained from biodiesel production is a big challenge as this crude glycerol cannot be used for direct food and cosmetic applications.

The total biodiesel capacity worldwide increased to 59.5 million tonnes in 2008 and this trend is expected to continue Potentially 6 million tonnes of glycerine is thus generated worldwide in biodiesel production, causing a global glut of glycerol as industrialised nations move to substitute fossil fuels with more sustainable alternatives. Glycerol production in the United States already averages more than 350,000 tons per year and in Europe production has tripled within the last ten years. Currently disposal of surplus glycerol in Europe is by largely by incineration (2007) or, on a smaller scale, composted. In some of the biodiesel market countries like Germany, crude glycerol is almost treated as waste and pays for its disposal (Frost and Sullivan 2008a).

The current market conditions have made it difficult for most biodiesel producers to realize economic benefits through the sale of their main by-product. However, businesses and researchers around the globe are currently engaged in research and development projects, with the primary goal of developing economically viable technologies capable of utilizing this overabundant resource.

The objective of the project is to present alternative solution for economical-technological sustainable utilisation of the glycerol co-product which accompanies oil-derived biodiesel. These products are carbon neutral and can support both the energy, agricultural and chemical sectors on their goals towards sustainability.

2 Glycerol Properties

Glycerol is a chemical compound, 1, 2, 3-propanetriol, also commonly called glycerin or glycerine. Its name originates from the Greek word glykys, meaning sweet. In its pure form it is a colourless, odourless, viscous liquid that is widely used in pharmaceutical formulations. For human consumption, glycerol is classified among the sugar alcohols as a caloric macronutrient. Glycerol has three hydrophilic hydroxyl groups that are responsible for its solubility in water and its hygroscopic nature, i.e., it absorbs water from the air. This property makes it valuable as a moistener e.g. in cosmetics and food. The compound is highly functional and thus it reacts with organic and inorganic acids to form aldehydes, esters, ethers and many derivatives. Glycerol is heavier than water (density is 1.26 kg/l (25 °C)) and is miscible with both water and ethanol. The non-toxic and biocompatible compound melts at 17.8°C and boils with decomposition at 290°C.

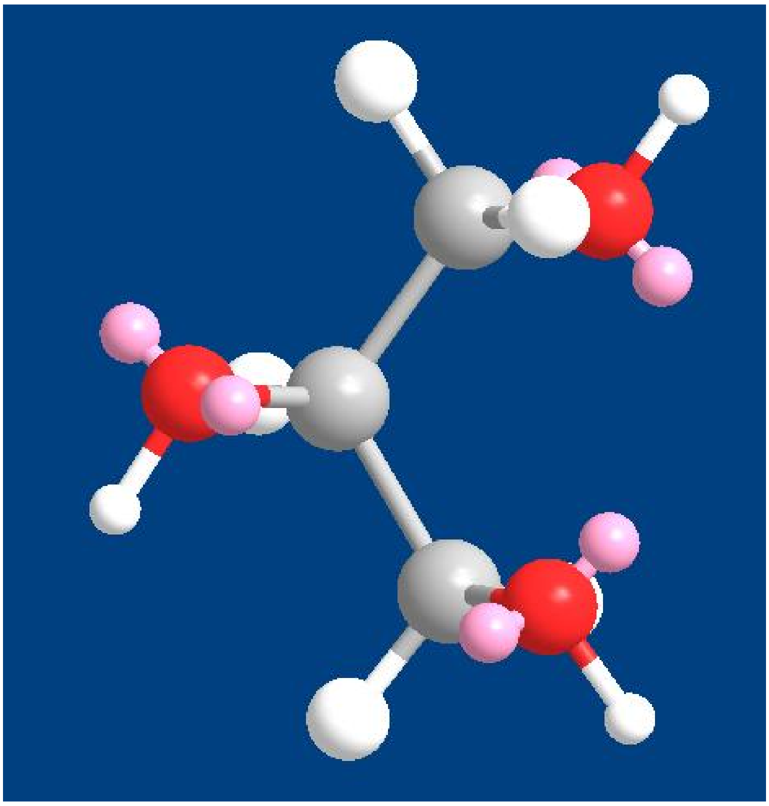

Figure 1. Glycerol

3 Glycerine markets

In 2008, the total glycerol market in terms of volumes, produced from three different processes of transesterification (biodiesel), saponification and hydrolysis, was 3.46 million tonnes.

The volume expected to be used in the technical industry in 2011 is 2 million tonnes. The total glycerol market in 2011 is expected at almost 5.1 million tonnes. In 2011 only 40 % of the crude glycerol produced will be utilised and the remaining 60 % will be considered as oversupply (Frost & Sullivan 2008a).

In 2008, Europe and Asia-Pacific accounted for over 55 % of the global glycerine market. At the moment Europe is the largest market for glycerine in the world (GIA 2008).

Current glycerine consumption in Europe is estimated at 395 000 tonnes and is growing fairly slowly at ca 1.7 %/a. (2001-2010). Until last year the Asia-Pacific was the engine room for growth in the market, with an annual growth rate of nearly 4.2 % over the same period. Especially China’s demand for glycerine has grown at a fast pace in the past decade.

Consumption of glycerine is expected to be strong due to consistent demand from the pharmaceuticals, personal care, and food and beverage segments. According to a report by Global Industry Analysts, a wide range of applications and the eco-friendly nature of products are the key factors driving market expansion (GIA 2008). Pharmaceuticals and personal care account for more than a third of the total market.

However, a large amount of glycerine products created as a by-product of the emerging biofuels industry has caused a dramatic commoditisation of the sector in recent years, driving prices down. Pharmaceutical grades of glycerine have also seen pricing pressure as a result of market oversupply.

There is a clear distinction between the markets for crude and refined glycerine. In 2008 there was oversupply of crude glycerol to the chemicals industry but the demand for refined glycerol was still growing. The volume of refined glycerol was not growing according to the demand growth. The growth of refined glycerol usage in the fine chemical industry is expected to rise creating a favourable market environment for the refined glycerol compared to the crude glycerol (Frost and Sullivan 2008a, Voegele 2009).

In 2007, 490,000 tonnes of *crude* glycerine were sold in Europe, and by 2013 the market is expected to reach volumes of 775 700 tonnes. In view of the biodiesel production driven by the support from the European Union and the governments of EU Member States, there would appear to be an oversupply potential of crude glycerine again towards the end of 2009. However, any change in the present situation is dependent on the support provided by respective national governments of EU Member States to the biodiesel industry (Frost and Sullivan 2008b).

In 2007, around 490,000 tonnes of *refined* glycerine were sold in Europe and it is expected that the refining capacity will increase at the rate of 4 % to reach nearly 633,000 tonnes by

2013. Newer applications and increased global demand from developing countries and especially from China, are factors driving the refined glycerine market. The glycerine refining companies are trying to target the international markets and are exporting the *refined* glycerine to countries like the US and China, where the demand in 2008 was still is high and the price that they can receive is better (Frost and Sullivan 2008b).

In September 2008, the spot price of tallow glycerol in North West Europe was 500-550 €/t FD[1]. Again the the price of crude glycerol had decreased under 100 €/tonne. Simoultaneously the spot prices in China and South-East Asia was somewhat higher 550-650 €/t FOB[2]. Crude glycerine was sold for ca 230 €/tonne (http://www.icispricing.com). The prices had decreased with ca 25 % from the year 2007 and an additional decrease is to be expected in 2009 (NAPM 2008).

The end application markets such as personal care, food, pharmaceutical and technical applications are quality-sensitive, and need high quality glycerine for production. Thus there is an intense competition in the refined glycerine market to supply the best and consistent quality of glycerine.

The increasing demand from end-users for refined glycerol has assisted in the growth of the total glycerol market. As the price of glycerol is low the industry is actively seeking new applications where refined glycerol could be employed. The result can be an increased demand for refined glycerol supporting the growth in the glycerol market Frost and Sullivan 2008a).

Table 1 and Table 2 provide the market drivers and restraints respectively ranked in order of impact for the glycerol market in the world for 2009 to 2015 (Frost and Sullivan 2008a).

Table 1. Glycerol Market: Market Drivers Ranked in Order of Impact (World), 2009-2015.

Rank	**Driver**	**1-2 Years**	**3-4 Years**	**5-7 Years**
1	Glycerol conversion to technical chemical can assist in the market growth	Medium	High	High
2	Increase in Biodiesel production worldwide	High	Medium	Medium
3	Increase in global demand for refined glycerol	High	High	High

Table 2. Glycerol Market: Market Restraints Ranked in Order of Impact (World), 2009-2015.

Rank	**Restraint**	**1-2 Years**	**3-4 Years**	**5-7 Years**
1	Oversupply of glycerol a major price restraint	High	Medium	Low
2	Future lack of government support to biodiesel projects could inhibit market growth	High	High	Medium
3	Refining capacity of crude glycerol is limited	Low	Medium	High

[1] Free Delivered
[2] Free On Board

4 Refining of crude glycerine

The recovered glycerol from biodiesel production reaction contains residual alcohol, catalyst residue, carry-over fat/oil and some esters. The glycerol from rendered feedstocks may also contain other impurities and other small concentrations of contaminants such as proteins or soaps, depending on the feedstock. Excess alcohol is due to the common practice of adding more alcohol and catalyst than is stoichiometrically required, in order to decrease reaction times. While it is often cost effective to recover the alcohol for reuse, it is difficult and expensive to purify crude glycerol for resale (i.e. remove water, catalyst, salt and other impurities), and continually falling pure glycerol prices make it cost prohibitive on a smaller scale.

The first step in physical refining is to remove fatty, insoluble or precipitated solids by filtration and/or centrifugation. This removal may require pH adjustment. Then the water is removed by evaporation. All physical processing is typically conducted at 65-90°C, where glycerol is less viscous, but still stable.

The crude glycerine is then upgraded to refined glycerol (99.7%) with vacuum distillation. The distillate is withdrawn at near boiling point and free from low volatile components before being bleached (Figure 1). Vacuum distillation of glycerol is a well-established technology but the disadvantage is that the process is capital and energy intensive. It is therefore best suited to operations > 25 tons per day.

Figure 2. Crude and refined glycerine (http://www.crowniron.com)

Ion exchange purification of glycerol is an alternative to vacuum distillation for smaller capacity plants. The ion exchange system uses cation, anion, and mixed bed exchangers to remove catalyst and other impurities. The glycerol is first diluted with soft water to a 15 - 35 % glycerol-in-water solution. The ion exchange is followed by vacuum distillation or flash drying for water removal, often to an 85 % partially refined glycerol (http://www.kpatents.com).

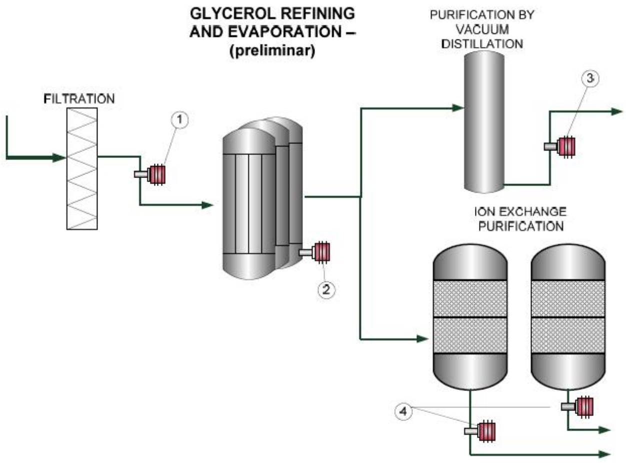

Figure 3. Example of glycerine refining equipment

Residue from the distillation, which typically includes the salt, organic matter and other non-volatile materials, can be discharged as a feed additive containing 10 – 15 % residual glycerine (http://www.crowniron.com).

5 Utilisation concepts

Glycerine has over 1,500 known end uses, both as a material in its own right, for example as a food ingredient or a plasticiser, and as a chemical building block for other materials.

Refined glycerol is mostly used in personal care applications. It is used as an emulsifier, emollient and conditioner. Glycerol is also used in food as a humectant, solvent and sweetener. It is used in the pharmaceutical industry as a humectant and also as a levigating agent. Glycerine is a main ingredient in technical products such as alkyd resins, polyether polyols and polyurethanes. The glycerol used in technical applications is growing because of its vast usage in production of epichlorohydrin, 1,3 propanediol and propylene glycol (Frost and Sullivan 2008a).

It is one of the major raw materials for the manufacture of polyols for flexible and polyurethane foams. It is also used as a plasticiser in cellophane and in the production of alkyd resins for paints and coatings. Glycerol is used to produce nitroglycerin, which is an essential ingredient of explosives and various munitions.

Other applications include the use of glycerine as a humectant in tobacco and for preparation of food products like cookies and cakes. Glycerine is also used widely in confectionery. In food applications refined glycerine is also used as a solvent, sweetening agent and as a preservative as glycerine is also an alcohol. The use in the food industry is expected to increase driven by a continuing trend towards lower fat content in foods.

In personal care applications, refined glycerine is used as an emollient, conditioner and emulsifier and is used for manufacture of products like soaps, toothpastes and skin care products like moisturising lotions. Based on an analysis made in the US 2006, the market growth in consumer products is especially strong. The aging population consumes more skin care cream and there is also a strong growth in sun screen lotions.

In the pharmaceutical industry glycerol is primarily used as a humectant and levitating agent and is used for preparation of products like cough syrup. Glycerine is also used in the medical industry as a drug for patients suffering from heart disease, due to its properties in vasodilation and reducing pressure on the heart.

Glycerine has also been used as a health supplement for sportsmen, to help in the process of hyperhydration. Glycerine is known to reduce the heart rate and also decrease the body's core temperature during conditions where the individual is exercising in conditions with high heat, thus it has a performance-enhancing effect in sports nutrition.

From 2005 onwards, there have been the developement of a number of new applications which have led to greater demand of glycerine. Amongst the notable new applications is a new process to manufacture epichlorohydrin from glycerine and also the use of glycerine for feed applications. Glycerine is a source of both tocopherols (vitamin E) and of lecithin, thus there is also an opportunity to use lecithin as an emulsifier within the food industry. These newer applications along with increased demand from conventional applications have led to an increased demand for refined glycerine in the market (Frost and Sullivan 2008a).

A great deal of current research is being conducted to try to make value-added molecules from crude glycerol (typically containing 20 % water and residual esterification catalyst) obtained from biodiesel production, as an alternative to disposal by incineration.

5.1 Energy utilisation

One alternative to disposal, particularly in association with biofuel production, is glycerol combustion as a heat source for the biofuel production process itself or separate CHP-production. Combustion of glycerol has been described as an elegant solution to the production of waste glycerol. Yet, many attempts to use waste glycerol as a heating fuel have had limited success and lacked real cost benefit.

Glycerol is more difficult to burn than conventional hydrocarbon fuels. While glycerol contains significant energy, its energy density is much less than conventional hydrocarbon fuels. The energy content of pure glycerine is about 19 MJ/kg, in comparison to that of kerosene, which is ca 43 MJ/kg. Glycerol is also a highly viscous liquid at room temperature, with a kinematic viscosity over 450 centistokes, whereas e.g. gasoline has a kinematic viscosity of 0.4-0.8. The high viscosity of glycerol makes it very difficult to atomize cold pure glycerol using standard nozzles found in fuel oil burners. Waste glycerol from biodiesel production may contain some alcohol which will lower the viscosity, but usually biodiesel producers prefer to evaporate and recover the alcohol from the glycerol for reuse. Glycerol can also be heated to radically reduce its viscosity. The main difficulty in burning glycerol is thus its high auto-ignition temperature. Glycerol has an auto-ignition temperature of 370^{o}C, as compared to 210^{o}C for kerosene.

Generally the energy value in crude glycerine is inadequate for successful start-up and continuous boiler operation. An accelerant (typically the alcohol used in the biodiesel manufacturing process itself) must be added in a proportion that improves combustion. Moreover the fuel must be raised to a temperature close to its native flashpoint (63^{o}C in the case of methanol).

When using crude glycerine as fuel, it is likely that metals Na or K, and metallic salts will contribute to the particulate matter emissions. “Crude glycerine contains 3-8 % of catalyst salts. The high level of residual salt in crude glycerine can cause hot corrosion in the combustion chamber and turbine. Thus particulate matter and coked material build-up inside the boiler require costly clean-up procedures and excessive downtime. Another concern is that glycerol might, unless it is properly combusted at high temperatures, release toxic acrolein fumes. These are mainly formed between 200 and 300 °C (Metzger 2007, Friis 2009).

5.1.1 Glycerol to power

One ton of glycerine produces approximately 1.7 megawatt-hours of electricity and approximately 2 megawatts of heat (Biodiesel magazine 9.12.2008). In spite of the difficulties mentioned above related to the combustion of glycerine, several companies are marketing burners designed to burn crude glycerol. To mentioned are e.g. Columbia, Centia ™ and GVE in US and UkrBioDiesel in Ukrainia http://www.ukrbiodiesel.com.ua). Bioking, located in the

Netherlands, sells a burner which can be run on a 50/50 mixture of crude vegetable oil and glycerol (www.bioking.nl). The immediate opportunity for these technologies is to use the waste glycerine stream from biodiesel plants as a fuel to provide plant process heat and to generate electric power.

One of the more recent newcomers on the market is UK-based Aquafuel Research Ltd which has developed a technology that allows crude glycerine to be burned in standard diesel generators used in combined-heat-and-power applications. The technology uses off-the-shelf diesel generators, which are altered slightly to use a new combustion cycle, which makes the diesel cycle independent of the fuel properties.

Most technologies are tolerant to water, methanol and non-glycerine organic compounds in the crude glycerine, which still usually needs to be desalted before combusted. The salts can be removed using commercially available equipment (Biodiesel magazine 9.12.2008).

5.1.2 Glycerol based fuel production

There are several ways to blend glycerol with solid biomaterial to improve the handling and calorific value of the fuel. Mixtures of e.g. coal and saw dust result in a fuel that is comparable with heating oil. The products are pastes or fuel brickettes. This fuel can be used in solid fuel boilers. Glycerol can also be mixed with lignin from the pulp industry for the utilisation in solid fuel boilers and gasification plants (Dravininkas 2005, Kemivärlden 2008).

Although blending glycerol with gasoline is a possibility, immiscibility of glycerol in gasoline hinders this option. Pachauri and He (2006) established specific component concentrations that keep a three-component (ternary) system consisting of gasoline, glycerol, and an amphiphile[3] in a single microemulsion phase making them miscible in each other. Propanol and ethanol were used as amphiphiles to make glycerol and gasoline miscible. This concept could be used by biodiesel producers to develop a co-product that could be blended with gasoline to make future biorefinery production economics more favorable (Fernando et al. 2007).

5.1.3 Glycerol as biogas feedstock

Glycerine may serve as a source of energy used in waste water treatment plant or manure digesters. The crude glycerine is typically added as a cosubstrate in proportions < 6-10 %. Higher proportions can cause process decline due to e.g. the build up of fatty acids. The optimum for the addition of glycerine for the biogas production from eg swine liquid manure is, according to research, in the range of 3 to 6 % by weight (

Glycerine is reported to increase biogas yields considerably. Cofermentation of both crude glycerol and soap water from the biodiesel production has also resulted in increased gas production yields. The theoretical gas production yield from soap-water and glycerol is 225 and 750 m^3/Mg respectively compared to eg. liquid manure (25 m^3/Mg) and waste grease (600

[3] a chemical compound possessing both hydrophilic and lipophilic properties.

m^3/Mg). However, as monosubstrates, the process becomes acidified and requires careful pH-control (Bockreis et al. 2008).

The biogas is used as fuel in diesel engines, which power electricity generators. Among others a Belgian biogas firm Organic Waste Systems (OWS) is now building a methane digester system that will use the crude glycerine coming from a large biodiesel producer who will use the resulting biogas to power its own plant (http://www.ows.be).

5.2 Converting glycerol to high-added value speciality chemicals

Glycerine can be used as a primary chemical building block and this sector presents interesting opportunities for the effective consumption of glycerine. When the cost of a chemical drops, its range of industrial utility broadens and the ability to absorb the cost of additional chemical transformations increases. Glycerine is currently facing this typical situation where its prices have declined and thus its range of use is widening. Glycerine is changing from its current state as an advanced intermediate or chemical end product to a starting material for a family of compounds.

Glycerine's multifunctional chemical structure can be exploited in different ways such as

- Selective oxidation of glycerol to form other intermediates
- Glycerol carbonate as a new solvent and product
- Glycerol as a component of new polymers
- Selective reduction processes
- Biochemical transformations

Economically most significant products are platform chemicals like *epichlorohydrin* and *1,3 propanediol*. Epichlorohydrin is a huge commodity chemical used in producing epoxy resins. The demand for epichlorohydrin as a commodity chemical is expected to be higher than its supply in 2010. Again 1,3-propanediol glycerine can be formulated into composites, adhesives, laminates, powder and UV-cured coatings, mouldings, novel aliphatic pol

yesters, co-polyesters, solvents, anti-freeze among other end uses. One of the most successful applications of 1,3-propanediol has been in the formulation of corterra polymers. As the production is limited and costs are higher, glycerol has become an attractive feedstock for production of for 1,3-propanediol (Frost and Sullivan 2008b).

Moreover various publications and patents present options for hydrogenating glycerol to *propylene glycol (1,2-propanediol*). The glycerine-based product is believed to have a cost advantage over conventionally produced propylene glycol. The low cost of raw glycerol is the reason why this concept is receiving so much interest also from large chemical actors such as Dow Chemical, one of the world's largest producers of conventional propylene glycol. Propyl glycol is used in a variety of product e.g. as anti-freezer (Chemsystems 2008).

A key concern in glycerine-to-propylene glycol processes is the suitability of the renewable propylene glycol produced for use in the various end uses, particularly personal care and food applications. For industrial applications renewable propylene glycol should be readily accepted. However, for most personal care and pharmaceutical applications extensive testing of this material will be required before this material is qualified for use.

Glycerol can be used as a feedstock for chemical and biological production of *hydrogen*. The main processes under research are catalytic reforming, microbial fermentation and pyrolysis and steam gasification of glycerol: these processes are still in a developing stage involving research on new catalysts improving the cost-efficiency of the process. As for microbial processes, high salt concentration in the crude glycerine decreases the production rate of hydrogen (Pachauri and He 2006, Cleantech 2007).

5.2.1 White biotechnology

By feeding glycerine to microbes, such as bacteria and yeasts, and allowing the microbes to use their natural genetic and enzymatic tools a number of value-added microbial products can be synthesized. The major part of these so-called white biotechnology innovations are still on the research or pilot stage and few have yet proceeded to commercial scale. Purification of glycerol from salts and non-glycerol residues is usually not required, but the glycerol needs to be sterilised in order not to contaminate the fermentation process.

New fermentation processes converts glycerine into formate, succinate, and other organic acids. This is a high-value feedstock that goes into a number of applications and is today manufactured largely from non-renewable resources (Frost & Sullivan 2008c).

Crude glycerine can also be used as the fermentation feedstock for microbial production of biosurfactants and bacterial polymers known as polyhydroxyalkanoates (PHAs). Each bioproduct is considered to be ecological as they are produced from renewable resources and can be quickly biodegraded upon disposal. The research has shown that in a number of these white biotech-processes the crude glycerine works better than pure glycerine to induce structurally distinct molecules for specific applications (Reuter 2009).

New innovations include technologies that convert natural glycerine, into propylene glycol that can be used to make antifreeze and other products. This product is a renewable alternative to petroleum-based propylene and ethylene glycols (SDA 2006). Moreover, in Sweden, a process for the production of dihydroxyaceton (a pharmaceutical ingredient) from glycerol has been brought into commercial scale (Engelmark 2006).

5.3 Livestock and agricultural applications

5.3.1 Cultivation

Crude glycerol has in combination with citric acid been used for the manufacturing of biodegradable weed barriers and sticky films intended to hold grass seeds on the ground long enough to germinate. This provides an ecologically friendly ways to fight weeds and grow grass (Rosner 2007). Diluted glycerol solutions can also be used as stimuli for cultivation of grain for seed. This is method is used e.g. in rural areas in Russia (Kemivärlden 2008).

Glycerol also may be used as antifreeze for plants, if mixed with water in a 10 % solution. It is believed to be effective at temperatures down to -18°C.

5.3.2 Animal feed fortification

While the price of raw glycerol is decreasing, crude glycerol may find an important application in animal feeds. As a fodder additive one main concern is the possible animal health risks of methanol residues in the crude glycerol.

Crude biodiesel glycerol has been tested as a supplement in feed for laying hens, broilers, and swine. The trials showed that feeds containing up to 10 % crude glycerol have little to no adverse effect on laying hen egg production or broiler body weight gain. The same level of crude glycerol added to swine feed showed little or no adverse change to pig body weight gain, carcass composition, and meat quality (Frost and Sullivan 2007). Hansen et al. (2009) suggested restricting inclusion of glycerol to dietary levels less than 8 %. Furthermore, levels of methanol and ash residues should be monitored to prevent excessive amounts of these compounds in pig diets (methanol 1.83 % of crude glycerol).

Glycerol of different purities can be included in mixed diets for ruminants up to 10 % of the dry matter as a substitute for rapidly fermentable starch sources, e. g., wheat or tapioca, without negatively affecting ruminal environment, ruminal nutrient turnover and whole-tract digestibilities of organic matter constituents (Shröder and Südekum 1999).

The Food and Drug Administration in US has established an upper level of 150 ppm for methanol in animal feed, which correspond to 1 - 1.5 % methanol in crude glycerol, in case of 8-10 % inclusion (Mooney 2008).

5.3.3 Livestock products fortified with Omega -3 fatty acids

Virginia University in US recently reported a novel fermentation process using microalgae to produce omega-3 fatty acids from crude glycerol. Crude glycerol functions here as a carbon source for microalgae, which are natural “factories” for omega-3 fatty acids. The purpose is to use the omega-3 fatty acid rich algae as an animal feed.

The utilisation of algae as feed for a variety of livestock is currently under investigation. If successful, it opens up possibilities for the production of fish, chicken meat and eggs and milk products fortified with heart-healthy omega-3s. As the typical Western diet often lacks omega-3 fatty acids this would not only provide more options for health-conscious consumers but also giving livestock producers a way to add value to their products. The concept has been proven in e.g. fish cultivation. Fish fed the algae contained significantly increased amounts of omega-3 fatty acids (Voegele 2008b).

Figure 4. Juvenile cobia fed with omega-3 fortified algae to fish in an aquaculture facility, at Virginia Cobia Farms in Saltville. http://www.cals.vt.edu/news/pubs/innovations/jan2009/biodiesel.html

6 Summary and Conclusions

The rise in biodiesel production over the last decade means that the market can no longer absorb all the extra glycerol. Biodiesel producers are to find alternative means for disposing of crude glycerol, which by rule is expensive to purify for industry use.

Glycerine is also increasingly being used in technical applications. It is likely that there will be industrial processes in the future which will take in crude glycerine as the input. Glycerine is also being used as a substitute for propylene glycol, which has the same applications, as that of glycerine. The low price is interesting to many companies and thus a focus on R&D is observed to strive to exploit glycerine within new applications. The demand for refined glycerine is then expected to rise as newer applications are being identified.

The following table gives an overview of possible glycerol utilisation concepts and their application area.

Table 3. Glycerol utilisation concepts.

Application	Technology maturity	Applicability for Crude / Refine	Increased value
Glycerol to power	Commercial tech.	Crude (desalting required)	+
Glycerol based fuel production	Commercial tech.	Crude (ev. desalting)	+
Glycerol as biogas feedstock	Commercial tech.	Crude	+
Converting glycerol to high-added value speciality chemicals	Commercial tech.	Refined	+++
Platform chemicals	Commercial tech.	Refined	++
Food industry	Commercial tech.	Refined Very high purity	+++
Pharmaceutical applications	Commercial tech	Refined: Very high purity grade	+ + +
Glycerol to hydrogen	Research stage	Crude / refined	++
White biotechnology	Research, few commercial technologies	Crude (sterilisation required)	+++
Agriculture - cultivation	Practical applications	Crude	+
Animal feed fortification	Practical applications / research (depending on the stock)	Crude	+
Livestock products fortified with Omega -3 fatty acids	Pilot stage	Crude (sterilisation ev. required)	++

It is important to take into consideration that over 95 % of all current glycerol applications use refined glycerine. The end application markets will be important partners in developing large scale glycerine consumption processes. Hence it will be important to determine the effect of glycerine purity on the various conversion processes undertaken.

The amount of refining and marketing of additional products can add complexity and cost, but also can increase potential revenue streams to the operation. Purification equipment is expensive and its feasibility is to be carefully considered. The implication of the development of new glycerine based products and chemical does make glycerol refinery a more attractive option compared to previous years. A feasibility study is required to define e.g. the minimal refining capacity for economical operation.

For smaller scale glycerol production, the concept of cofermenting crude glycerol with waste water sludge, biodiesel soap water and other locally available organic waste streams is a sustainable concept combining both glycerol utilisation and local waste management to produce local fuel (biogas). Also the use of crude glycerol as food additive is a relatively easy utilisation concept not requiring investments in glycerol refinement. Here the analysis and control of the crude glycerol, especially with regard to its methanol content, is necessary.

Just like petroleum refineries make more than one product that are the feedstock for other industries, the same will have to be true for biofuels. Innovative uses for the byproduct of biodiesel production, glycerol could help transform the biodiesel industry into something that more closely resembles the petroleum industry, in which fuel is just one of many profitable products.

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

Deliverable 2
The Role of Antioxidants in the Production of Fish Biodiesel

Revision	Organization	Date & Visa	Due date of the Deliverable
Written by	Elina Merta VTT		
Checked by			
Validated by	VTT		

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)	

Summary

Biodiesel is a common name for methyl esters derived from different fats and oils. Biodiesel is produced by transesterification process where alcohol, typically methanol and an alkaline catalyst are needed. Transesterified oils can be used in standard diesel engines without any modification. Waste fish oil can be used as raw material for transesterification. However, depending on the separation methods, fish oil usually requires some pre-treatment to remove the typical impurities of raw fish oil e.g. water, fish residue and saline compounds.

The main challenge with fish oil biodiesel its low oxidative stability. In biodiesel oxidation the methyl esters convert to alcohols, ketones, aldehydes and as the final step, to insoluble gums. These may cause severe damage in equipment utilizing the fuel.

The low oxidative stability of fish oil biodiesel is mainly due to high content of polyunsaturated fatty acids. The standard method for testing the oxidation stability of biodiesel is the Rancimat test or Oxidation Stability Index (OSI) which is an accelerated oxidation test in a controlled temperature (110 °C). According to European standard EN 14214 the minimum acceptable OSI (induction period) is 6 hours based on Rancimat test. However, based on previous investigations the fatty acid composition of pangasius fish oil may differ significantly from marine fish oil. The lower share of polyunsaturated fatty acids may improve the stability compared to other fish oil biodiesel grades.

Antioxidants can be used to prevent or slow down oxidation of biodiesel. The most common synthetic antioxidants are phenolic type compounds such as TBHQ, BHA or BHT. The antioxidant dosage needed is influenced e.g. by the initial OSI, fatty acid composition, presence of natural antioxidants and storage conditions.

There are several commercial antioxidants available for stabilization of biodiesel. Most commercial antioxidant products are proprietary mixtures of several antioxidants having synergistic effect. The suitability of antioxidants for a certain biodiesel grade and the proper dosage has to be determined by laboratory testing.

Altogether seven plants producing fish oil biodiesel are presented in this study. The plants are located in Scandinavia, North America, Honduras and Vietnam. Unfortunately, very limited information was available through the companies on their use of antioxidants. For the selection of suitable antioxidant for Enerfish demonstration plant, testing with the actual fish oil is needed.

There are a couple of examples on the use of commercial antioxidants with fish oil biodiesel. These include Finnish Rovina (Ionol BF 200) and Scandinavian MBP Group (BioSINEOX 100) More over, the use of a common food and feed antioxidant exthoxyquin has been tested (Alaska, test). The experiences are generally good. However, some disadvantages which mainly relate to the storage conditions of antioxidant have been reported. Considering the further studying and testing with biodiesel derived from pangasius waste oil, pure antioxidants TBHQ, PY and PG could be considered as well. For the final selection of

antioxidant, experiences from the Vietnamese fish biodiesel plants, Agifish and Minh Tu, would be especially useful.

Based on the information available, the European price of commercial antioxidants varies between 6 and 10 €/kg. Depending strongly on the dosage needed, the cost of antioxidant could be between 1 and 6 c/l biodiesel. However, the amount of active ingredient as well as the efficiency of product on a certain biodiesel grade varies greatly making the comparison of prices complicated.

The commercial antioxidant products covered in this report are produced by companies with European or US origin. However, most of these companies have offices or subsidiaries in Asia. The logistics of antioxidants must be considered carefully with the Vietnamese partners and antioxidant vendors in order to keep freight costs reasonable. In addition, especially pure antioxidants with no specific brand name could be best available through local manufacturers or vendors.

Contents

Terminology and abbreviations

Antioxidant	A molecule which slows down or prevents the oxidation of other molecules. In biodiesel industry they help in achieving the product stability level required. Antioxidants may be of natural origin or they can be chemical additives.
BHA	Butylated hydroxyanisole. The compound is a mixture of two organic compounds, 2-*tert*-butyl-4-hydroxyanisole and 3-*tert*-butyl-4-hydroxyanisole. Can be used as antioxidant.
BHT	Butylated hydroxytoluene. Can be used as antioxidant.
Biodiesel	Fuel produced by transesterification from renewable sources and with fuel properties equivalent to petroleum diesel. Can be used in diesel engines without modification.
DHA	Docosahexaenoic acid (C22:6). One of the major components of omega-3 polyunsaturated fatty acids.
FFA	Free fatty acids. Fatty acids are carboxylic acids with a long unbranched carbon chain. When fatty acids are not attached to other molecules, they are known as free fatty acids.
EPA	Eicosapentaenoic acid (C20:5). One of the major components of omega-3 polyunsaturated fatty acids.
FAME	Fatty Acid Methyl Ester. Term generally used for biodiesel produced by transesterification.
OSI	Oil Stability Index
PG	Propylgallate. Can be used as antioxidant.
PUFA	Polyunsaturated fatty acid. Usually used to describe fatty acids containing > 3 double bonds.
PY	Pyrogallol. Can be used as antioxidant.
TBHQ	Tert-butylhydroquinone. A phenolic organic compound which is used to prevent various oils, fats and food from oxidation (antioxidant).

7 Introduction

Agricultural biofuels represent today ca. 2-3 % of the world's total energy need. However, the share of biofuels is likely to grow during the next years and decades as climate change mitigation proceeds. In 2007 the European Union set a binding target of increasing the level of renewable energy in the overall EU consumption to 20 % by 2020. EU also instructed that 10 % of transport fuel consumption in the EU area should be bio-based by 2020, meanwhile ensuring the sustainability of biofuels used. The price of crude oil is also rising which will further increase the interest in alternative fuels. (Piccolo 2008; EC 2007)

The growing share of biofuels in the global energy consumption will require assessment of its sustainability as well as economic factors. Most of the conventional raw materials for biofuels are vegetable oils which are at the same time food products. The widespread production of biofuels from e.g. rapeseed oil, palm oil, corn or other food raw materials will have a strong impact on world's food chain. Also the intense farming of these raw materials for fuel use may affect water resources, land use, deforestration and global markets. Thus the sustainability of biofuel raw materials is a fundamental question to be answered in order to ensure their acceptability as a tool in climate change prevention. (Piccolo 2008) The price of biodiesel and thereby its competitiveness in the fuel market is strongly dependent on the price of oil used as raw material. Therefore the selection of most feasible raw materials is crucial for biodiesel industry. (Lin and Li 2009)

The abovementioned issues encourage us to survey new non-food raw materials for biofuels. Various waste materials represent an appealing alternative as their use as biofuel raw material would generate several benefits. Aquatic wastes are one of the interesting options to be considered. Oils extracted from fish waste can be utilized to produce biofuels. (Piccolo 2008)

The goal of the Enerfish project is to demonstrate a novel distributed energy production system applicable for aqua producers. Cleaning waste of a fish processing plant is used to produce raw material for biodiesel. The demonstration will take place at a fish processing plant, Hiep Thanh Seafood Joint Stock (HT-Food) in Vietnam. This report concentrates on fish oil biodiesel, its stability and the chemicals for improving the stability. Furthermore, the applicability of different antioxidants for the demonstration plant is discussed considering local conditions.

8 Fish based biodiesel

According to FAO statistics, in 2006 world's fisheries produced nearly 52 million tons of fish, crustaceans, molluscs, etc. by aquaculture (FAO 2006). The discarded parts of fish, e.g. viscera, eyes, fins, tails, represent roughly 25 % of the fishery production (Lin and Li 2009). This material is low-cost and readily available in many coastal and riverside areas where aquaculture is abundant.

The use of fish gut and other fish based waste as a raw material for biodiesel has been under intensive research in the past few years. The technology itself is not new, and the process is quite simple. Fish oil extracted from fish waste is used as the raw material of biodiesel process. The yield of the process may as high as 1 l biodiesel / 1 kg of fish waste. The technology is applicable especially to small scale and local energy production and could be utilized at basically any fairly large aquaculture farm and even in large fishing trawlers. As well as environmental benefits the production of fish oil biodiesel would present social benefits for the community, e.g. increased employment. (Piccolo 2008) However, the poor stability of fish oil and fish based biodiesel presents a major challenge.

8.1 Production

The most common production technology for biodiesel is transesterification which can be used to produce fish based biodiesel as well. In transesterification, bio-based oil is turned into a form suitable for diesel engines. This process will be utilized also at the Enerfish demonstration plant at HT-Food in Vietnam. The process equipment will be delivered by Preseco Oy.

The transesterification process is depicted in figure 1. Before the actual process, crude oil analysis takes place. Based on the analysis results right quantities of process chemicals can be used in the process. The oil is transferred into an esterification tank together with the chemicals, methanol and NaOH, which acts as a catalyst. Oil is mixed and recycled in the tank in order to begin the esterification process. In the end of process, glycerol and crude biodiesel are present in the tank as two layers. Glycerol is transferred into its own container and the crude biodiesel is conveyed into a washing unit where the biodiesel is cleaned from any impurities. (Preseco 2009)

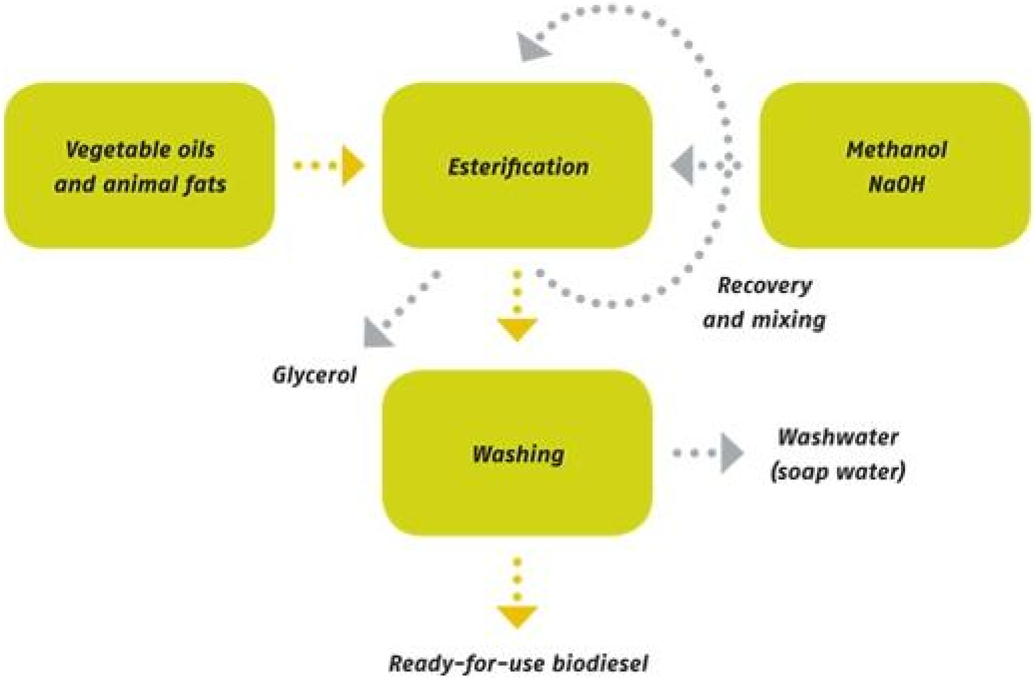

Figure 5. Preseco biodiesel production process using transesterification (Preseco 2009).

The properties of the resulting biodiesel depend on the raw material used. E.g. the characteristic odour and the resistance to cold are features that are dependent on the raw material. Typically, the fatty acid composition does not change in transesterification process. The resulting biodiesel is a mixture of long-chain fatty acid methyl esters (FAMEs). (Preseco 2009; Dunn 2008)

Due to possible variations in raw material quality, the uniformity of the product is a challenge in biodiesel production. Other possible risks relate to process safety issues; the transesterification process generates some hazardous gases and compounds (methanol and NaOH or KOH) that are inflammable and explosive. However, the Preseco process is fully closed and consequently no gases will exit the process. (Preseco 2009) The waste management and the utilization of by-product glycerol are also questions to be taken into account. Thus, professional process design and operation are essential.

8.2 Fish oil biodiesel properties

The quality of waste derived biodiesel varies greatly by the raw material. Therefore it is essential to determine the properties of the biodiesel in question for evaluating its suitability for a specific purpose. The properties of biodiesel can be described by various parameters. In the following discussion the properties of fish oil biodiesel are divided into the ones that relate to biodiesel as fuel, environmental aspects and properties concerning the oxidation stability.

8.2.1 Fuel properties

The fuel properties of biodiesel are characterized by parameters typically used for petrodiesel as well. These include cetane number, flash point, ash and water content, heating value, density, viscosity etc. Cetane number indicates the quality of the compression ignition of diesel fuel. Large cetane number for diesel means shorter ignition delay, less knocking and lower formation of nitrogen oxides. One of the challenging parameters for biodiesel is viscosity. The kinematic viscosity of biodiesel grades tends to be larger than that of petrodiesel thus causing increased risk of flowing problems in diesel engines. (Tang et al. 2008; Dinkov et al. 2009; Lin and Li 2009) Table 1 compares typical fuel properties of biodiesel from marine fish oil with the properties of commercial biodiesel from waste cooking oil.

Table 1. Fuel properties of biodiesel based on marine fish oil and waste cooking oil.(Lin and Li 2009)

Fuel property	Biodiesel from marine fish oil	Biodiesel from waste cooking oil
Acid number (mg KOH/g)	1.17	0.69
Specific gravity	0.86	0.87
Kinematic viscosity (cSt)	7.2 (at 40 °C), 4.4 (at 70 °C)	4.7 (at 40 °C)
Cetane index	50.9	48.1
Flash point °C	103	141
Carbon residue (wt-%)	0.76	0.26
Heating value (MJ/kg)	41.37	40.11
Element oxygen (wt-%)	7.19	9.63

In general, biodiesel derived from animal fat, vegetable oil or used cooking oil has good fuel properties. Their flash point is high, lubricant properties are good and combustion efficiency superior compared to petrodiesel.

According to research done by Lin and Li (2009) on biodiesel derived from oil from a mixture of various marine fish, the cetane number of fish oil biodiesel was higher (50.9) than that of commercially available biodiesel (48.1) based on waste cooking oil. The higher cetane number can be explained by the larger share of saturated fatty acids in fish oil biodiesel. The heating value of fish oil biodiesel was around 41 MJ/kg. This is higher than the heating value of waste cooking oil biodiesel which is due to higher content of long-chain fatty acids in fish oil biodiesel. Flash point of fish oil biodiesel was observed to be 103 °C, which is lower than the flash point of vegetable oil biodiesel. However, the flash points of both biodiesel grades were higher than that of petrodiesel which can result in improved safety in fuel transportation and storage compared to petrodiesel. The amount of carbon residue of both biodiesel grades studied was lower compared to petrodiesel.

The kinematic viscosity of fish oil biodiesel is generally higher than that of biodiesel based on vegetable oil. The main reason for this is the higher content of saturated fatty acids in fish oil biodiesel grades. (Lin and Li 2009; Reyes and Sepúlveda 2006)

8.2.2 Environmental aspects

Fish oil derived biodiesel has excellent biodegradability. Combustion of biodiesel does not generate polyaromatic hydrocarbons (PAH) or nitrated polyaromatic hydrocarbons (nPAH). (Lin and Li 2009) Fish oil has its own characteristic features that require special consideration when utilizing fish oil in biodiesel production. These include the fatty acid composition and low oxidative stability of fish oil as described in chapter 2.2.3.

According to tests done in diesel engines in Alaska, carbon monoxide and particulate emissions of burning fish oil biodiesel are lower than those of fossil diesel. Meanwhile, nitrogen oxide emissions have been a few percents higher when using fish oil biodiesel. The heating value of fish oil biodiesel is slightly lower than that of petrodiesel. The thickening of fish based biodiesel in temperatures just below zero degrees celsius presented a challenge in Alaskan environmental conditions (Lee 2005, Lin and Li 2009). Reyes and Sepúlveda (2006) also recorded a reduction in PM-10 particulate emissions when burning fish based biodiesel compared to combustion of petrodiesel.

One of the possible risks in using fish oil as biodiesel raw material might be be the strong characteristic odour of the oil. However, in the study of Reyes and Sepúlveda (2006) no unpleasant odours were detected during the combustion tests of salmon oil based biodiesel and its blends. Experiences from a Finnish fish biodiesel company Rovina also promote this finding; no major problems with the biodiesel odour have been detected. According to Rovina, the odour of biodiesel is slightly fishy. Meanwhile, the exhaust gases from cars using fish oil biodiesel do not have any characteristic fishy odours. (Salminen 2009b) The experiences from MBP Group indicate that the odour of fish biodiesel resembles linseed oil. The combustion may generate a light fishy odour which has not been considered as problematic. (Bohman 2009)

8.2.3 Properties related to oxidation

One of the most vital factors influencing the feasibility of biodiesel as fuel is its oxidative stability. Oxidative stability can be evaluated by a number of indicators. The fatty acid composition of biodiesel reflects its oxidation characteristics; the higher the content of polyunsaturated fatty acids the higher the oxidation tendency. One of the oldest parameters to describe the level of total unsaturation of oil is the iodine value. However, this method has some cons that restrict its use. The analytics are tedious and more importantly, the results do not correlate with Oil Stabilation Index by Rancimat test which has been selected as the basis for European regulations on biodiesel stability. (Waynick 2005)

The standard method for testing the oxidation stability of biodiesel is the Rancimat test or Oxidation Stability Index (OSI) which is an accelerated oxidation test in a controlled temperature (110 °C). The method is described in EN 14112. In OSI analysis, oil sample is heated in a test tube purging it with a steady stream of dry air which bubbles through the sample. Oxidation products are drawn into a second tube which contains deionized water and a conductivity probe (figure 2). As the oxidation proceeds, volatile acidic compounds are formed and a slow rise in conductivity will be observed. At some point of time, there will be a steep rise in conductivity. The point with highest rate of conductivity increase is defined as

OSI. The period before this time point is defined as the induction period (IP). The requirements of EN 14214 standard on the fuel oxidative stability are based on Rancimat test results. In EN 14214 the minimum acceptable OSI (induction period) is 6 hours which has to be met at the production facility as well as at the fuel station where the vehicles are fuelled. (Lin and Li 2009; Dunn 2008; Waynick 2005)

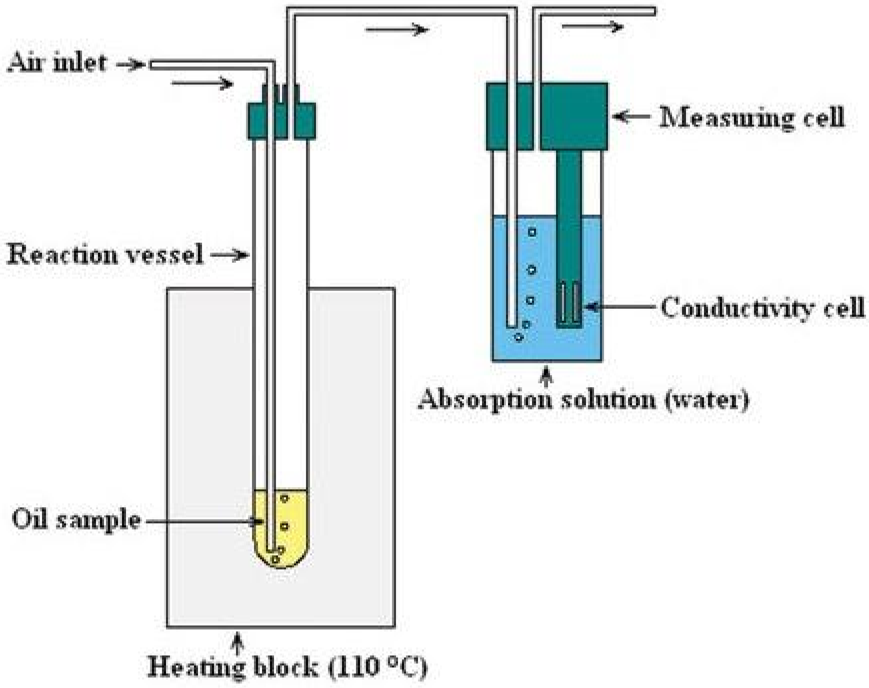

Figure 6. Schematic of Rancimat test setup (Steinbach 2007).

Peroxide value is another parameter to determine the level of fuel oxidation. In contrast to OSI where all volatile acidic compounds formed in the oxidation chain are measured, peroxide value only detects the primary oxidation products, hydroperoxides. However, it has been shown that peroxide value and OSI values correlate well with each other. (Waynick 2005)

The amount of free fatty acids (FFA) in biodiesel feedstock also reflects the auto-oxidation level of the material and is an important parameter considering the reaction kinetics and FAME yield in transesterification process. The FFA content of oil can be characterized by acid value. (Lin and Li 2009; Aryee et al. 2009; El-Mashad et al. 2008)

Fish oil from marine fish normally contains plenty of omega-3 polyunsaturated fatty acids, whose main components are eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA). The carbon chains in fish oil are generally longer than in vegetable oils. Depending on the separation methods, fish oil usually requires some pre-treatment before using it in biodiesel production because raw fish oil typically contains impurities, such as water, fish residue and saline compounds. Pre-treatment may include e.g. adsorption of impurities, winterizing (storage in cold conditions), centrifuging and washing. (Lin and Li 2009)

Table 2 compares the main components of two kinds of fish oil biodiesel and commercial biodiesel derived from waste cooking oil (vegetable oil).

The overall compositions of marine fish oil biodiesel and salmon oil biodiesel are similar, e.g. when considering the amount of long carbon-chain fatty acids. The share of saturated fatty acids is also larger in both fish based biodiesels than in vegetable based biodiesel. Also El-Mashad et al. (2008) reported similar results (ca. 27 % saturated fatty acids) in their study on waste salmon oil.

Furthermore, as shown in table 2, the amount of polyunsaturated fatty acids (>3 double bonds in carbon chain) was found to be close to similar in both fish based biodiesel grades. As a general rule, biodiesel grades with plenty of polyunsaturated fatty acids are susceptible to oxidation. Premature oxidation of fuel will easily lead to precipitation and thereby possible problems in engines using this type of fuel. (Lin and Li 2009)

Table 2. The comparison of fatty acid composition (w-%) of marine fish oil biodiesel, commercial waste cooking oil based biodiesel and salmon oil biodiesel (Lin and Li 2009; Reyes and Sepúlveda 2006).

Fatty acid	**Chemical structure**	**Biodiesel from marine fish oil (Lin and Li 2009)**	**Commercial biodiesel from waste cooking oil (Lin and Li 2009)**	**Biodiesel from salmon oil (Reyes and Sepúlveda 2006)**
Myristic acid	C14:0	3.16	0.54	5.08
Pentadecanoic acid	C15:0	-	-	0.45
Palmitic acid	C16:0	**19.61**	**14.18**	**15.39**
Heptadecanoic acid	C17:0	1.82	0.17	0.46
Stearic acid	C18:0	5.24	3.77	4.00
Nonadecanoic acid	C19:0	-	-	0.08
Arachidic acid	C20:0	4.75	0.8	0.15
Behenic acid	C22:0	1.55	0.1	0.09
Myristoleic acid	C14:1	-	-	0.16
Palmitoleic acid	C16:1	5.16	0.74	7.55
Heptadecaenoic acid	C17:1	-	-	0.79
Oleic acid	C18:1	**20.94**	**47.51**	**20.76**
Nonadecaenoic acid	C19:1	-	-	0.42
Eicosaenoic acid	C20:1	-	-	2.33
Docosaenoic acid	C22:1	0.98	0.18	0.92
Tetracosaenoic acid	C24:1	-	-	0.42
Hexadecadienoic acid	C16:2	-	-	1.03
Hexadecatrenoic acid	C16:3	-	-	0.19
Linoleic acid	C18:2	2.69	**24.83**	3.78
Linolenic acid	C18:3	0.9	4.97	0.99
Octadecatetraenoic acid	C18:4	-	-	1.27
Eicosadienoic acid	C20:2	0.81	0.17	0.3
Eicosatrienoic acid	C20:3	-	-	0.3
Eicosatetraenoic acid	C20:4	2.54	0.38	2.08
Eicosapentaenoic acid (EPA)	C20:5	3.7	0.03	9.49
Heneicosapentaenoic acid	C21:5	-	-	0.54
Docosatetraenoic acid	C22:4	3.86	0.14	0.3
Docosapentaenoic acid	C22:5	2.44	0.05	4.94

Docosahexaenoic acid (DHA)	C22:6	**15.91**	0.04	**13.99**
Total saturated fatty acids		**37.06**	**19.77**	**25.7**
Total mono-unsaturated fatty acids		**26.35**	**48.37**	**33.35**
Total polyunsaturated fatty acids (>3 double bonds)		**28.45**	**0.64**	**32.61**
Total long carbon-chain fatty acids	**C20-C24**	**37.7**	**1.99**	**39.52**

The oxidation level of fuel, defined by the peroxide number, has been found to be lower in fish oil based biodiesel than in commercial vegetable oil biodiesel. This can be explained primarily by the larger share of saturated fatty acids in fish oil biodiesel. However, the rate of increase in the peroxide number, i.e. the oxidation rate, was higher in fish oil biodiesel than in commercial biodiesel. This is due to the higher content of polyunsaturated fatty acids (PUFAs) that contain several double bonds. These fatty acids are prone to self-oxidation reaction. (Lin and Li 2009)

Generally the FFA content of fish oil increases with increased storage time, even at low temperatures (Aryee et al. 2009). Free fatty acids in crude bio-based oil may significantly decrease the yield of biodiesel in the transesterification process and may result in soap formation when reacting with the alkali catalyst. High initial FFA concentration can be reduced by acid-catalyst treatment, which turns the free fatty acids into esters. A high acid value may significantly affect the economy of fish oil based biodiesel production. (El-Mashad et al.2008)

8.3 Need for antioxidants

Biodegrability of biodiesel brings simultaneously benefits and disadvantages. The fuel is safer for the environment since the possible spills will biodegrade more readily. However, the premature degradation of biodiesel is unwanted and may cause severe damage in equipment utilizing the fuel. As showed in chapter 2.2.3 fish oil based biodiesel is prone to oxidation, mainly due to its relatively high content of polyunsaturated fatty acids, such as EPA and DHA. The oxidation of fish oil biodiesel will lead to formation of unwanted secondary reaction products such as alcohols, aldehydes and acids. The formation of acids will increase the acid value of biodiesel. Finally oxidative linking of fatty acid chains may occur resulting in higher molecular weight polymers. These will increase biodiesel viscosity and formation of sticky, insoluble gums. Therefore, oxidation of biodiesel may cause detrimental effects in engines and in fuel fuel feeding systems. (Waynick 2005; Dunn 2008).The principle of biodiesel oxidation process is depicted in figure 3 where R’ is a carbon-based free radical, ROO’ is a peroxy radical and ROOH is hydroperoxide.

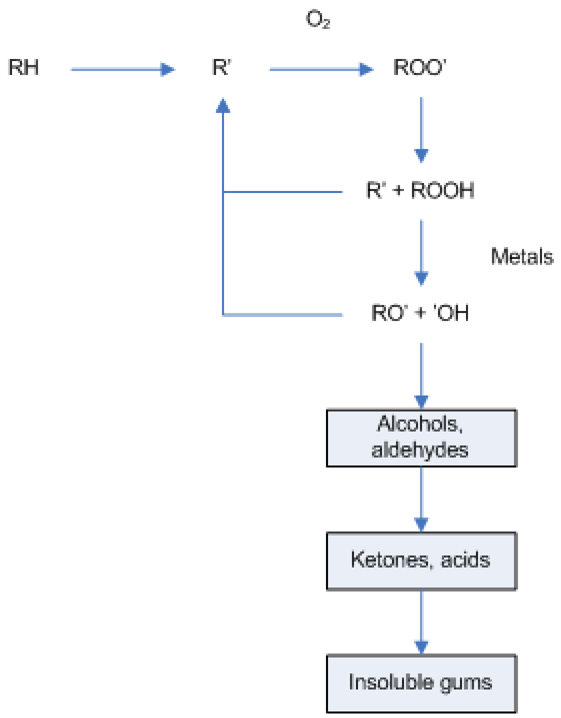

Figure 7. Reaction mechanism of biodiesel oxidation (reproduced after Albemarle 2006)

Generally, transportation and utilisation of very vulnerable biodiesel grades, such as fish oil biodiesel, should be designed bearing in mind the risk of oxidation. Fish oil biodiesel should preferably be utilised rather quickly avoiding excessive storage periods.

Biodiesel oxidation is promoted by several factors including presence of metals (Cu, Fe, Ni, Sn, brass) or other oxidation promoters such as free fatty acids, high temperatures, presence of light and availability of oxygen. Also the type of alcohol used in transesterification process may have an impact on the oxidability of biodiesel; longer chain alcohols might produce biodiesel with better stability. (Waynick 2005; Dunn 2008)

Oxidation of biodiesel can be prevented by modifying the physico-chemical storage conditions of the product in an advantageous way. Storage under inert nitrogen atmosphere retards the oxidation of biodiesel. Also the material of the storage container may have an effect on the biodiesel stability. Glass containers have been shown to improve biodiesel stability to a certain extend. Also, the separation of shorter chain fatty acids and partial hydrogenation of remaining fatty acids would result in improved fuel stability. However, these methods require fairly large investments in storage or fractionation equipment. Also, these special storage solutions are challenging with respect to biodiesel logistics. By far, the most feasible method for preventing biodiesel oxidation is the addition of suitable antioxidant. (Dunn 2008)

The need for antioxidants is determined by the initial oil stability index (OSI) of the biodiesel, the raw material, processing and storage conditions, possible contaminants present and how quickly the biodiesel is consumed. (Eastman 2008b) The antioxidant chemistry, the available chemicals and their suitability for fish oil biodiesel is discussed in chapter 3.

The challenge with many synthetic antioxidants is their possible adverse effects on the environment if spills happen. Often, the chemicals are not readily biodegradable and thus may cause risk of bioaccumulation. Also, considering occupational health and safety, some precautions are usually required to ensure the safe use of these chemicals. Therefore, there is a need to develop more biodegradable and less harmful chemicals that would still be effective enough in protecting biodiesel.

9 Antioxidants for biodiesel preservation

Antioxidants are chemicals that prevent or slow down the oxidation process. Based on their reaction mechanisms, antioxidants can be divided into chain breaking and hydroperoxide decomposers. Currently, the investigations on the preservation of fatty oils have concentrated on the chain breaking type of antioxidants. The most common chain breaking antioxidants applied in the biodiesel industry are the phenolic-type compounds. Typically, the biodiesel industry prefers synthetic antioxidants over antioxidants from natural sources. This is mainly due to the higher efficiency of synthetic antioxidants. (Waynick 2005; Dunn 2008) The reaction mechanism of chain breaking antioxidants can be described as in equation 1. (Waynick 2005)

$$ROO\cdot + AH \rightarrow ROOH + A\cdot$$

$$A\cdot \rightarrow \text{Stable products} \qquad \textit{Equation 1}$$

The antioxidant (AH) contains a highly unstable hydrogen that is easily abstracted by a peroxy radical formed in fatty acid oxidation. The resulting antioxidant radical (A·) is stable or reacts to from a stable molecule that does not contribute to chain reaction. (Waynick 2005)

Based on results from various studies, addition of antioxidants does not cause adverse changes in other biodiesel properties than the acid value. According to Schober and Mittelbach (2004), acid value increased significantly with higher antioxidant concentrations. Thus, it is recommended to use lowest possible concentrations of antioxidant for biodiesel stabilization in order to minimize all possible side-effects.

Generally, dosages under 1000 ppm are for most chemicals enough to protect biodiesel (Dunn 2008). However, there are various factors influencing the actual antioxidant dosage needed. The different fatty acid compositions, the possible presence of natural antioxidants, the environmental conditions mentioned in chapter 2.3 and the varying effectivity of each antioxidant on the biodiesel in question determine the adequate dosage (Tang et al. 2008).

Usually, the antioxidant has to be added to biodiesel in a very early phase of biodiesel life. That is, antioxidants are not effective if oxidation has already propagated too far neither can they return the oxidation products into their original FAME form. (Eastman 2008b)

The synergistic effect of different antioxidants is utilized in many commercial antioxidant products designed especially for biodiesel stabilization. These products are often mixtures of two or more antioxidants. (Dunn 2008) There are several published studies on the applicability of commercial antioxidant chemicals on biodiesels based on different feedstocks. A range of chemicals commonly used as biodiesel antioxidants and their applications are listed in table 3. Even though many commercial antioxidant products contain more than one chemical, pure "one-chemical" antioxidants are available as well. Many of these chemicals are food-grade products.

Table 3 Antioxidants for biodiesel stabilization

Antioxidant	Chemical composition	Properties	Applications, biodiesel raw materials	References
BHA	butylated hydroxyanisole	Waxy, white to yellowish solid, soluble in alcohol, insoluble in water	poultry fat, palm oil	Tang et al. 2008; Dunn 2008
BHT	2,6-di-tert-butyl-4-methylphenol	Crystalline solid, soluble in alcohol, slightly soluble in water	poultry fat	Tang et al. 2008
TBHQ	tert-butylhydroquinone	White crystalline solid, soluble in alcohol, slightly soluble in water	soy bean oil, cotton seed oil, yellow grease used frying oil, rapeseed oil, sunflowerseed oil, tallow	Tang et al. 2008; Mittelbach and Schober 2003; Dunn 2008
DTBHQ	2,5-di-tert-butyl-hydroquinone	White to tan crystalline solid, soluble in alcohol, insoluble in water	rapeseed oil, used frying oil	Schober and Mittelbach 2004
α-Tocopherol		Clear, light yellow to amber oily liquid, soluble in alcohol, insoluble in water	soy bean oil	Dunn 2008
PY	pyrogallol	White crystalline solid, soluble in alcohol, soluble in water	soy bean oil, cotton seed oil, yellow grease, poultry fat, used frying oil, rapeseed oil, sunflowerseed oil, tallow	Tang et al. 2008; Mittelbach and Schober 2003; Dunn 2008
PG	propylgallate	White crystalline solid, soluble in alcohol, very slightly soluble in water	soy bean oil, cotton seed oil, yellow grease, used frying oil, rapeseed oil, sunflower oil, tallow, palm oil	Tang et al. 2008; Mittelbach and Schober 2003; Dunn 2008

Generally, the effect of antioxidants depends on the biodiesel feedstock. According to studies, the different effects of antioxidants can be explained by their chemical structure. All antioxidant types studied contain an aromatic ring with different functional groups. The active hydroxyl groups donate protons that interrupt the oxidation process by reacting with free radicals. The electronegativity of antioxidants is therefore one important factor influencing its effectiveness. (Tang et al. 2008)

According to a study by Mittelbach and Schober (2003) PY, PG and TBHQ were the most effective antioxidants for biodiesels derived from rapeseed oil and used frying oil. For sunflower oil based biodiesel largish dosages (1000 ppm) of PY or PG resulted in good stability. This was explained by the authors by the high content of unsaturated linoleic acid (18:2) in sunflower oil. Tallow methyl ester, which contains very little natural antioxidant, is naturally rather unstable. PY was the most suitable antioxidant for this type of biodiesel. According to many studies TBHQ, PY and PG seem to be effective for the widest range of biodiesel feedstocks.

9.1 Antioxidant suitability for fish based biodiesel

The selection of suitable antioxidant is crucial for the improvement of biodiesel stability. Several studies show that the effectivity of antioxidant chemicals varies greatly between FAME's derived from different feedstocks. (Schober and Mittelbach 2004; Tang et al. 2008; Mittelbach and Schober 2003; Dinkov et al. 2008) Thus, the optimal selection of chemical is not always straightforward. Unfortunately, there is no open literature on the application of antioxidants to stabilize fish oil biodiesel.

Fish oil typically is rich with polyunsaturated fatty acids such as DHA and EPA which are easily oxidized. This is why biodiesel derived from fish oil has low natural stability. Yet many fish species contain natural antioxidants that provide some protection for the fish oil. The reddish colour of salmon and trouts is due to astaxanthin, which is classified as carotenoid. Astaxanthin is a powerful antioxidant that in nature originates from the fish's prey, e.g. krills and plankton. For cultured salmonids astaxanthin is supplied as feed-additive in order to improve to colour. (Choubert et al. 2009) Navarro-Garcia et al. (2004) characterized different ray species e.g. considering their antioxidant content. Considerable amounts of carotene and α-tocopherol were detected in the fish oil. These compounds are lipophilic in nature and therefore they are extracted with the oil. However, according to studies the biodiesel process removes at least a part of the oil's natural antioxidants (Waynick 2005; Witmer et al. 2007).

In a study by Yoshihiro et al. (1986) the stability of sardine oil rich with EPA (32.8 %) and DHA (14.8%) was investigated. It was found out that the oxidation rate of fish oil was lower than that of pure unsaturated fatty acids, linoleic (18:2) and linolenic (18:3) acids alone. The researchers concluded that natural antioxidants might protect sardine oil from oxidation therefore slowering the oxidation rate compared to pure polyunsaturated fatty acids.

The demonstration biodiesel plant in the Enerfish project will utilize waste from catfish (*Pangasius hypophthalmus*) processing. The main product of the fish processing plant is catfish fillet. The fat content of the waste is ca. 22 %. In contrast, the lipid content of the actual product, fillet, is low, typically being less than 2 wt-%. The fatty acid composition of *P. hypophthalmus* fillets is dominated by saturated fatty acids (45 % of total fatty acids). Monounsaturated fatty acids, mainly oleic acid (C18:1), represent ca. 35 % of fatty acids. However, the total share of polyunsaturated fatty acids (> 1 double bond) is only around 15 % of the fatty acids. The main polyunsaturated fatty acid species present in *Pangasius* fillets are linoleic acids (C18:2), arachidonic acid (C20:4) and DHA (22:6), which represent ca. 7.9%, 2.1% and 2.7% of the total fatty acids, respectively. The content of omega-3 fatty acids in *Pangasius* fillets is very low compared to many other fish species and fish products. (Orban et al. 2008)

Thi Thuy et al. (2007) analysed catfish by-products (animal feed) originating from Mekong Delta of Vietnam. The by-products consisted of fish heads, bones, skin and meat scraps and they were processed to either dry or wet feed for animals or aquaculture. Altogether seven individual products from different facilities were investigated. According to the fatty acid analysis, the main species of all catfish based animal feed products were palmitic acid (C16:0), stearic acid (C18:0) and oleic acid (C18:1) representing ca. 30-35%, 8-10% and 32-39 % of the total fatty acid content, respectively. The share of each fatty acid depended mainly on the feedstock used; only minor effect was reasoned to be due to the processing method used. A summary of the fatty acid composition of pangasius fillets and by-products is presented in table 4 below.

Table 4 Fatty acid compostions of pangasius products including the main fatty acid species (Orban et al. 2008; Thi Thuy et al. 2007)

Fatty acid	Chemical composition	Pangasius fillet (stored frozen)	Pangasius by-product (head and bone by-product feed)
Myritic acid	C14:0	4.77	3.96
Palmitic acid	C16:0	28.19	33.44
Stearic acid	C18:0	11.17	9.74
Palmitoleic acid	C16:1	1.64	1.78
Oleic acid	C18:1	31.01	36.11
Eicosenoic acid	C20:1	1.05	1.29
Linoleic acid	C18:2	7.87	6.47
Eicosatetraenoic acid	C20:4	2.11	-
Docosahexaenoic acid	C22:6	2.67	-

Based on the data presented above, some preliminary conclusions can be made on the suitability of antioxidants for preservation of biodiesel derived from pangasius cleaning waste. The fatty acid composition of Vietnamese pangasius seems to be exceptional compared to most fish species. The share of saturated fatty acids is large both in fillets (Orban et al. 200) and in pangasius by-products (Thi Thyu et al. 2007). Also the amount of monounsaturated fatty acids is relatively high. In contrast, the polyunsaturated fatty acids (PUFA), especially omega-3 fatty acids represent a strikingly low percentage of the total fatty acids when comparing to the results from other fish species (e.g. table 2 in chapter 2.2.3).

Due to these differences, some inequality in the oxidative behaviour of pangasius biodiesel versus marine fish oil biodiesel might be expected. The high oxidation rates observed with fish oil biodiesel might not be seen with pangasius oil biodiesel since the amount of PUFA's is lower. In fact, the fatty acid profile of fish oil derived from pangasius waste might be closer to some type of vegetable oil or tallow than marine fish or salmon. This might be beneficial in the stabilization of the biodiesel produced from pangasius waste as conventional antioxidants may be effective in protecting this type of biodiesel. TBHQ and PG and PY are antioxidants suitable for a wide range of vegetable oil biodiesel grades (table 3). These chemicals have successfully been applied to biodiesel grades from less stable raw materials, such as used frying oil. Therefore it might be expected that these chemicals would be efficient in improving the stability of fish oil based biodiesel as well. However, experimental studies are needed to determine the actual composition of pangasius oil fatty acids and the suitability of antioxidants for the final product.

9.2 Commercially available antioxidant products

There are several commercially available synthetic antioxidants that can be utilized to protect biodiesel from unwanted oxidation. These products contain various types of chemicals with different reaction mechanisms. Most commercial products are complex mixtures of antioxidant chemicals and a number of additives. Therefore, the assessment of the suitability of certain commercial product for a certain biodiesel grade is virtually impossible without appropriate testing and evaluation.

9.2.1 IONOL ® BF

One of the commercially available antioxidant trademarks is IONOL® BF manufactured by Raschig (http://www.raschig.com/en). The product family consists of several individual products with varying effectivity on different feedstocks. The antioxidative effect of IONOL® BF products is based on the ability of the chemical to interrupt the oxidation chain reaction in biodiesel. The chemical captures the free radicals as they from and therefore the self-feeding oxidation chain is interrupted. For fish oil based biodiesel the manufacturer's representative recommends IONOL ® BF 300 which is a new, effective product. However, this product is not yet commercial. Another product from the IONOL BF series, IONOL® BF 200, has been successfully applied on a Finnish facility manufacturing fish oil biodiesel (Rovina 2008). (Sjöblom 2009)

The cost for a small amount of Ionol BF 200 in Europe would be around 7 €/kg. The dosage of antioxidants will have to be evaluated by laboratory tests. Based on experiences from a Finnish fish biodiesel facility, dosage of 1000 ppm would probably not be enough to secure biodiesel stability. However, 1000 ppm can be used to estimate a preliminary cost of antioxidant. On the European price level, the daily antioxidant cost for 13 000 kg of biodiesel would be ca. 90 €. Of course, in practice the pricing of the product will depend e.g. on the port of delivery and the order quantity. (Sjöblom 2009)

According to manufacturer's representative, IONOL BF 300 would also be a strong candidate for fish biodiesel antioxidant. The dosages needed would most probably be smaller than those of IONOL BF 200. The cost of BF 300 on European price level would be ca. 7.9 €/kg which is a little higher than the cost of BF 200. (Sjöblom 2009)

IONOL ® BF 300 is a sterically hindered phenolic antioxidant, in which the size or shape of functional groups hinders the reactions of phenolic group. The prevalent active ingredients in the product are 2,6-di-tert-butylphenol and ethoxyquin. In the material safety data sheet the product is marked as harmful (Xn) and it may cause long term adverse effects on the environment (R53). The product is a liquid and solvent free antioxidant with 100 % active ingredient. IONOL ® BF 300 breaks the oxidation chain reaction by trapping the free radicals. The product remains uncrystallized even at low temperatures. According to the manufacturer IONOL ® BF 300 is soluble in all tested types of biodiesel, at any concentration. For used cooking oil biodiesel ca. 260 ppm is enough to double the stability from 6 to 12 hours in the Rancimat test. With this antioxidant addition, the biodiesel fully complies with the requirements of standard EN 14214 (oil stability index minimum of 6 hours). However, the recommended dosage for fish waste biodiesel would have to be determined based on oxidation stability tests. The pricing of the product will depend on the delivered amount and location. Deliveries to Vietnam are possible. (Raschig 2008; Gillmann 2009)

9.2.2 BioExtend 30

BioExtend 30 is Eastman Chemical Company's antioxidant product for biodiesel markets (http://www.eastman.com/). BioExtend 30 contains 30% mono-tert-butylhydroquinone (MTBHQ) which is known to be a powerful antioxidant. The product also contains 1.5% citric acid which acts as a chelating agent. Citric acid additionally enhances antioxidation by binding metals which, if available, can catalyze the oxidation of biodiesel. The speciality of the BioExtend product is this dual system with synergistic effect. The physical form of BioExtend product is a yellow liquid with flash point of 46°C. BioExtend 30 can be used in temperatures ranging from -25°C to 40°C and it is therefore suitable for cooler climates as well. The product is a ready-to-use solution enabling simple feeding systems with typical stirring time of 10 minutes. Typical dosages of BioExtend 30 are 100-500 ppm depending on the source and quality of the biodiesel as well as the targeted oil stability level. According to the manufacturer BioExtend 30 is suitable for biodiesel produced from for example soy, rapeseed, sunflower and palm oil. The efficiency of the product is claimed to be superior compared to other antioxidants, such as butylhydroxytoluene (BHT), or MTBHQ alone. (Eastman 2007; Eastman 2008a, Eastman 2008b)

In addition to the active ingredients mono-tert-butylhydroquinone and citric acid, BioExtend 30 also contains butyl acetate and diethylene glycol monobutyl ether. In the material safety data sheet BioExtend 30 is classified as harmful (Xn), dangerous for the environment (N) and very toxic to aquatic organisms (R50/53). (Eastman 2008c)

9.2.3 Baynox ®

Lanxess (http://corporate.lanxess.com/en/) manufactures two different antioxidants for the biodiesel industry: Baynox® and Baynox®plus. The products are supplied either as pure solid active ingredient or as ready-to-use solution containing 20 m-% of active ingredient dissolved in biodiesel. In Baynox® product the active ingredient is butylhydroxytoluene (BHT) thus being a phenolic type of antioxidant. Baynox® traps the hydroperoxides formed during biodiesel oxidation and hinders the process from proceeding. Baynox® is suitable for biodiesel from vegetable oils with a low content of multiple unsaturated fatty acids and having an iodine number <120. Raw materials for such biodiesel are e.g. rapeseed, palm oil, used cooking oil and animal fats. Typical dosages of Baynox® are 300-400 ppm. For biodiesel containing high levels of double and triple unsaturated fatty acid esters a stronger product, Baynox® Plus, is recommended. The active ingredient in Baynox® Plus is 2,2'-methylenebis(4-methyl-6-tert-butylphenol). According to tests run by Lanxess, dosages of 250-350 ppm Baynox® Plus are needed to improve the stability of soy bean biodiesel to the level required in EN 14214. Baynox® Plus is more suitable also for biodiesel based on sunflower and jatropha oils. Baynox® products do not contain sulphur, nitrogen or any corrosive compounds. (Lanxess 2006; Lanxess 2007; Lanxess 2008)

According to Lanxess' representative, a general rule is that standard antioxidants designed for rape and soy biodiesel are not efficient enough to ensure the quality of fish oil biodiesel. Lanxess recommends Baynox ® Plus with an estimated dosage of 1000 to 2000 ppm (0.01-0.02 %) for fish oil biodiesel. The final dosage depends on the unsaturation level and the purity of the biodiesel. At least one small scale plant in Canada is using Baynox ® Plus to stabilize fish oil biodiesel. (Ingendoh 2009)

The approximate cost of Baynox ® Plus will be around 10 € /kg, depending on the ordered amount and site. Lanxess ships its products worldwide. The shipments to Vietnam would be organized by Lanxess' subsidiary in Singapore. (Ingendoh 2009)

According to the material safety data sheet, Baynox ® Plus may cause long-term adverse effects in the aquatic environment (R53). (Lanxess 2006)

9.2.4 ETHANOX

Albemarle (http://www.albemarle.com/) produces antioxidants for biodiesel and fossil fuels. Alltogether seven different products in the ETHANOX series are marketed as suitable for biodiesel stabilization (4701, 4702, 4733, 4737, 4740 and 4760E). The latter four are delivered in liquid form. ETHANOX antioxidants prevent biodiesel from oxidation by trapping the radicals formed in the chain reaction. For example ETHANOX 4740 is a blend of several antioxidants having synergistic effects and it is suitable for less stable biodiesel. ETHANOX 4702 is a strong antioxidant which is recommended for highly oxidation sensitive systems. By their chemical nature Albemarle antioxidants are either hindered phenolics (4701, 4733, 4737) or blends of hindered phenolic and phenylenediamine (4740). (Albemarle 2005; Albemarle 2006; Albemarle 2008)

The manufacturer preliminary recommends Ethanox 4760E for fish oil biodiesel. According to Albemarle's experience Ethanox 4760E is efficient in a large range of biodiesel feedstrocks, e.g. soybean, animal fat and recycled frying oil. Typical dosages are between 300 and 600 ppm. Ethanox 4760E is liquid in room temperature. According to the material safety data sheet, Ethanox 4760E is marked as corrosive (C) and dangerous for the environment (N, R51/53). (Van Oudenhove 2009; Albemarle 2008b)

A preliminary cost estimate for the product is 6 €/kg. Using dosage of 600 ppm as an example would lead in daily antioxidant costs of ca. 47 €. This price is FCA, and therefore the freight costs are not included. The product could be shipped to Vietnam from the company's warehouses in USA or in Antwerp.

9.2.5 BioSINEOX ™ 100

AACF (Antioxidants Aromas and Fine Chemicals (Pty.) Ltd.) (http://www.aafc.co.za/) is a South African company producing hindered phenolic antioxidants for various applications. Their product for biodiesel stabilization is BioSINEOX™ 100 which contains a proprietary blend of TBHQ, DTBHQ, BHT, chelants and solvents. The range of antioxidant chemicals presents a synergistic effect. The product is sold as 100% active ingredient powder, thus, it is not diluted. However, the product dissolves to biodiesel quickly. BioSINEOX™ 100 is suitable for a wide range of biodiesels, including highly unstable biodiesel and biodiesel/petroleum diesel blend. The product does not contain any sulphur or nitrogen and according to manufacturer, low dosages are required (typically 200 ppm). The product has hazard symbols harmful (Xn) and dangerous to the environment (N). (AACF 2008)

There are experiences on the use of BioSINEOX 100 with fish oil biodiesel in Scandinavia. (chapter 4.4). The product is available e.g. through a Norwegian representative, Arcon As.

9.2.6 Kemin BF

Kemin (http://www.kemin.com/) is an international nutritional ingredient manufacturer, whose product range also includes antioxidants for the biodiesel industry. Their Kemin BF product combines antioxidant tert-butylhyroquinone (TBHQ) and metal chelator citric acid. Hence, the active ingredients are similar to BioExtend 30 by Eastman and the reaction mechanisms are alike as well. Kemin BF series comprises two products, Kemin BF 320 and BF 310. Both are suitable for stabilizing vegetable oil biodiesels and are delivered in liquid form. Typical dosage of BF 320 is 150-500 ppm. BF 310 can be used when added chelation is needed and normal dosages range from 300 to 750 ppm. Neither of the products contains nitrogen, sulphur or metals and they solubilize completely in biodiesel and blends. The material safety data sheets of the products were not available. Figures 4 and 5 demonstrate the increase in biodiesel stability when using the Kemin BF antioxidant. (Kemin 2008)

Kemin has Asian offices in China, India and Singapore. The price information on the products was not available.

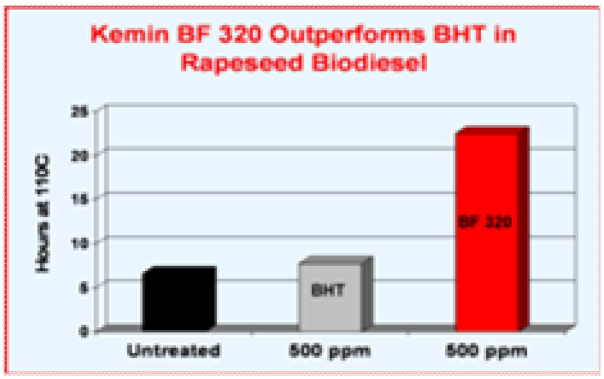

Figure 8 (Kemin 2008)

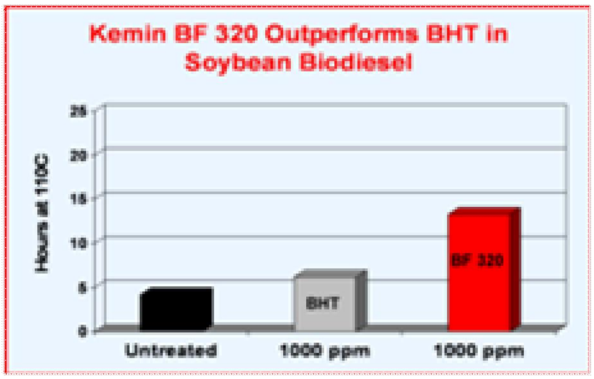

Figure 9 (Kemin 2008)

10 Case studies on the production and use of fish oil biodiesel

In order to get a more realistic picture on the production of fish oil biodiesel and the use of different antioxidants, practical knowledge was gathered from facilities producing fish oil biodiesel. This was carried out by direct contacting of facilities and exploring company www pages. Following case studies present the information on the identified fish biodiesel facilities.

10.1 Rovina, Finland

Rovina (http://www.rovina.fi/) is a Finnish company established in 2005 in the city of Uusikaupunki. Rovina produces biodiesel mainly of wish gut and other fish waste. The product can be used as such e.g. as heating oil in oil heating systems of industrial facilities, farms and private households. Rovina is constantly seeking new possibilities for processing other by-products of food industry into biofuels. (Rovina 2009)

The raw material for biodiesel production is pre-treated fish gut from which the oil is extracted by separation. The process operates as a batch type transesterification reactor having a capacity of 4500 l/crude oil/batch/day. The process yield is 85-90 % depending on the quality of the crude oil. (Salminen 2009)

The antioxidant used at Rovina is Ionol BF 200 which is locally delivered by Algol Chemicals Oy. The chemical was selected based on the tests done by the vendor. The dosage of 6 ml/l biodiesel is needed to ensure the biodiesel's oxidative stability for 6 months. According to Rovina the antioxidant product in question is expensive (1 c/ml). However, based on price information on other products the price of Ionol BF 200 is close to average. An additional rise in operating costs at Rovina is caused by the storage of antioxidant in a separate heated space built only for this purpose. The main advantage of using antioxidant is that the company is able to give 6 months' shelf life guarantee for the produced biodiesel. The product is environmentally hazardous, inflammable and may cause skin irritation. Furthermore the use of the antioxidant is rather difficult since it crystallizes in temperatures below 25 °C. This presents quite a challenge in Finnish environmental conditions. (Salminen 2009)

In addition to its own biodiesel production, Rovina also manufactures devices and equipment for handling fish gut. Rovina Fish Power is a ready-to-use treatment plant for waste produced at fish farms. The plant is built in 40 ft sea container and it is easy to transport and place at the desired location. The capacity of the plant is ca. 1000 kg of fish cut per hour. A storage tank of 25 m^3 can be located above the container. The end products of the process are fish oil, solid animal feed and water. Animal feed can also be delivered to a biogasification plant if desired. The plant is self-sustaining in heat energy due to the fish oil that can be used to produce energy for the plant as well as external needs. Along with producing heat and animal feed the process also provides an efficient way of handling problematic fish waste on site. (Rovina 2008)

10.2 UniSea, Alaska

The community of Unalaska in Alaskan Aleutian islands is located southwest of mainland Alaska. Seafood, mainly pollock, processing is an important industry in the area and vast amounts of fish oil are produced every year as by-product of fish processing. Over half of the fish oil produced in the area is consumed at the producing facilities as a boiler fuel and remainder is sold outside Alaska for use in animal feed, aquaculture and as human dietary supplements. However, considering the high transportation costs and the local need of electricity, it would be advisable to make use of the fish oil locally as a fuel for electricity generators. (Steigers 2002)

In 2001 the seafood producer, UniSea, Inc. (http://www.unisea.com/) producing 15 000 to 57 000 liters (ca. 13 000 to 51 000 tons) of fish oil daily, started a state-funded demonstration project to test the use of blended fish oil and diesel as generator engine fuel. The fish oil was used as such, without processing it to biodiesel. The blends were used to generate heat and electricity at the company's processing facility. The fish oil was found to be substantially more viscose and slightly more acidic than conventional diesel. The oil also has lower lubricity and a higher flash point than diesel fuel. (U.S. Department of Energy; Lee 2005; Steigers 2002)

Different fish oil to diesel ratios were tested in a 2.2 MW 2-cycle Fairbanks Morse engine generator. The use of fish oil blends did not cause any major problems in the engine. Starting the engines from either warm or cold condition was accomplished even easier than with pure diesel. Also shutdowns were accomplished without difficulty. An increase in engine- mounted fuel filter pressure was observed due to the higher viscosity but this did not cause any problems for the engine. No unusual wearing or deposits were detected in the equipment during the nearly 8000 hours' operation with fish oil blend. However, the variations in the fish oil quality could possibly generate some problems. The standard purification practises in the fish oil producing facilities may not be adequate to ensure the fish oil's quality for wide-spread use in engine generators. Increased protein, water or sediment load in the oil might cause difficulties in fuel purifiers and filters at the consuming site. Therefore, it is advisable to have centrifugal fuel purifiers or applicable filter devices on site to ensure the oil quality. (Lee 2005; Steigers 2002)

According to the experiences from this project, fish oil and diesel blends produce lower overall emission, especially particulate emissions, but the NOx emissions are slightly higher than with diesel fuel. According to Unisea the fish oil /diesel blends do not generate any unpleasant fishy odours. After the first piloting, the company has successfully continued using 50/50 blends of fish oil and diesel in larger scale. (U.S. Department of Energy; Lee 2005; Alaska Energy Authority 2009; Steigers 2002)

However, more sophisticated engines cannot usually utilize fish oil as such or even as blended with diesel. Therefore, the Alaskan project has continued with fish oil based biodiesel which has been tested at Denali National Park. This project, which took place in 2005, is described in the below chapter.

10.2.1 Denali National Park

A 55 kW generator using fish biodiesel originating from the Unalaska area operated at the Denali National Park and Preserve maintenance and housing facility. Prior to testing at Denali National Park, a smaller generator using the same fuel had been successfully run at the University of Alaska Fairbanks. According to results from the project, biodiesel worked well in a variety of situations and the National Park Services is interested in this new fuel. Also, a blend of fish oil and petrodiesel has been tested in a few park vehicles. (Ahern 2005)

According to tests done at University of Alaska Fairbanks, the processing of fish oil to biodiesel removes the natural antioxidants present in the raw fish oil. Due to this, the resulting biodiesel is prone to oxidation and can have detrimental effect on the engines. The research group has experiences on severe damage in engines, especially fuel pumps, because of oxidized biodiesel. Adding of antioxidant ethoxyquin to biodiesel in a dose of 400 ppm was sufficient to retard most oxidation. Ethoxyquin is a food grade antioxidant which was chosen for availability reasons. The research team also tested the use of non-transesterified fish oil in diesel engines. Even partially oxidized fish oil could be utilized after pumping the fish oil through a packed bed of kitty litter. This treatment removed the part of the fish oil that formed the polymers and thereafter the oil could be used to run diesel engines on blends of 20% and 50% (fish oil in diesel). However, long-term effects of fish oil on equipments still remain unclear. (Witmer 2009)

10.3 Ocean Nutrition Canada

Ocean Nutrition Canada Limited (ONC) (http://www.ocean-nutrition.com/) is a company based in Nova Scotia, Canada. The company develops, manufactures and markets omega-3 based ingredients derived from fish oil. The company's product portfolio includes dietary supplements and food additives in a patented micro-capsule powder form. (Ocean Nutrition Canada 2009)

Since 1999 the company has been using waste oil to make biodiesel for the use in the boiler and heating systems in the company's Mulgrave facility. Furthermore, the company has started to sell the excess biodiesel to a local gas station chain which blends it into B20 (a mixture composed of 20% of biodiesel with 80% of diesel) before selling it. (Eco-Efficiency Centre 2004; Faludi 2007) Information on the use of antioxidants at ONC was not available.

10.4 MBP Group

MBP (http://www.mbpgroup.eu/) is a European company whose business comprises the processing of various industrial by-products. The company's business lines include animal feeds, biofuels, fertilizers and technical oils. The biodiesel production facility is located in Norway. (Bohman 2009; MBP Group 2009)

One of the raw materials MBP is using for biodiesel production is the fish oil which comes as by-product from Omega 3- oil industry using marine fish mackerel. The production of biodiesel is ca. 6000-7000 tonnes/year of which around 75% derived from fish oil. As the raw material comes from human dietary nutrient production, the oil is also very pure and contains little impurities. According to company's representative, they can use practically every type of fat or oil to produce biodiesel, however, the high quality and purity of oil is essential. The fish oil raw material of MBP contains some water and therefore the resulting biodiesel water content is just on the limit of EN 14214 (maximum of 500 mg water/kg). Therefore, the company calls the product as Biodiesel Non-standard. The product is used in logistics vehicles, e.g. lorries. According to company's representative, there have not been any problems with the fish biodiesel odour. A slightly fishy odour may occur in combustion. (Bohman 2009)

To stabilize the fish oil based biodiesel, MBP has successfully used BioSINEOX 100 antioxidant. The product has been selected based on testing and other factors, such as pricing. (Bohman 2009)

10.5 Aquafinca

Aquafinca Saint Peter Fish is located in Honduras near Santa Cruz de Yojoa. The company farms and processes tilapia and in addition produces biodiesel from the fish waste. The estimated production rate of biodiesel is over 11 000 litres a day. The biodiesel is used in electricity production at the company's own facilities and also in vehicles including lorries and buses. (Piccolo 2008) Information on the use of antioxidants at Aquafinca was not available.

Figure 10. Process equipment for biodiesel production at Aquafinca, Honduras. (Piccolo 2008)

10.6 Agifish Co. and Minh Tu Ltd Co.

The Mekong Delta is an important area for fish farming and processing and therefore large quantities of fish waste are produced as well. Agifish (http://www.agifish.com.vn/home_en/modules/news/) is one of the Vietnamese catfish producers. The company has agreed to set up a joint venture with Saigon Petro in order to establish large-scale production facilities of biofuel from catfish gut. Two local refrigeration firms are involved in the project as well. The production capacity of the plant is planned to be 30 000 tonnes of fuel a year and it would be located in An Giang province. A feasibility study is being prepared and negotiations on investments are underway. Possible plant-sites are still being evaluated as well. The processing equipment is planned to be imported. Converting fish waste to valuable fuel could generate major opportunities for rural communities by providing income as well as securing energy supply. However, according to Agifish representative, Vietnamese biodiesel producers have not yet received any state fundinge for biodiesel production. (Piccolo 2008; Vietnam News 2008)

Minh Tu Ltd Co. is another Vietnamese company that plans producing fish oil based biodiesel. In 2006 the company successfully investigated and the possibilities to manufacture biodiesel. The company has invested in building a facility and partners with domestic companies as well as a Cambodian company. It is estimated, that the facility could produce as much as 2 million litres of biodiesel a year. The company affirms that 50/50 blends of biodiesel and mineral diesel would be feasible. Minh Tu Ltd Co. purchases its raw material through local agencies and the company has a stable supply of 50 tonnes of catfish fat a day. The price of catfish fat has recently risen steeply which presents a challenge to biodiesel industry. This is due to the fact that local enterprises are exporting large volumes of catfish fat. Therefore, Minh Tu Ltd co. is considering the use of jatropha oil for the production of biodiesel. (Vietnam News 2008)

According to Vietnamese biodiesel producers, there are some tedious procedures and legal limitations for biodiesel which hinder the use of biodiesel. Yet, there are no clear national requirements on biodiesel quality. However, a draft of biodiesel quality standard has been prepared. (Vietnam News 2008)

10.7 Application of antioxidants at HT-Food

Based on the preliminary analysis, the production of biodiesel at HT-Food demonstration plant will be ca. 13 t/d. The antioxidant will be added to biodiesel tank prior to leading the fuel in the cogeneration diesel power plant and other local diesel power plants. A suitable storage method for the antioxidant will still have to be selected. The possible options include e.g. a separate tank on site or delivery of antioxidant in sea containers. The choice will have to be made based on cost analysis, space limitations on production site, physical form of antioxidant etc. Generally, antioxidant in liquid form can be recommended because this eliminates the antioxidant dissolution phase from the process. The chemical nature of antioxidants will have to be taken into account especially considering the occupational and environmental safety issues as well as the technical requirements for the storage conditions. These issues have to be considered as the selection of antioxidant is completed.

There are several commercial antioxidant products available for stabilization of biodiesel. However, only few antioxidant producers or chemical vendors have previous experiences on biodiesel derived from waste fish oil. The final selection of antioxidant product and the determination of dosages needed require laboratory testing. Many chemical manufacturers offer services for this purpose. Product samples are usually available free of charge and some producers offer laboratory services to test the suitability and needed dosage of antioxidant based on Rancimat test.

The fatty acid composition is the main feature influencing the stability of oils and methyl esters. Based on the literature review done for this report, the composition of pangasius waste oil may show exceptional characteristic compared to e.g. marine fish oil. According to previous research, the share of polyunsaturated fatty acids in pangasius waste oil is lower than in marine fish oil which might indicate a better stability for pangasius waste oil. In practice, this could enable lower antioxidant dosages or the use of less-effective, and probably less costly, antioxidant products.

There are few examples on the use of commercial antioxidants with fish oil biodiesel. These include Finnish Rovina (Ionol BF 200) and Scandinavian MBP Group (BioSINEOX 100). Both companies have had good experiences with the products. However, Rovina reports some disadvantages which mainly relate to the storage conditions of antioxidant. In addition, an Alaskan study demonstrates the use of a common food and feed antioxidant exthoxyquin for stabilizing fish biodiesel. Considering the further studying and testing with biodiesel derived from pangasius waste oil, pure antioxidants TBHQ, PY and PG could be considered as well. For the final selection of antioxidant, experiences from the Vietnamese fish biodiesel plants, Agifish and Minh Tu, would be especially valuable.

Based on the information available, the European price of commercial antioxidants varies between 6 and 10 €/kg. On estimated dosages of 1 to 6 ml/litre of biodiesel, this would lead to antioxidant costs between ca. 1 and 6 c/l biodiesel. However, the amount of active ingredient as well as the efficiency of product on a certain biodiesel grade varies greatly making the comparison of prices complicated.

The commercial antioxidant products covered in this report are produced by companies with European or US origin. However, many of these companies have offices or subsidiaries in Asia. The logistics of antioxidants must be considered carefully with the Vietnamese partners and antioxidant vendors in order to keep freight costs reasonable. In addition, especially pure antioxidants with no specific brand name could be best available through local manufacturers or vendors.

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