Development and Application of Eco-friendly Oil Stimulant on Oil Spill Control Training

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Background & Motivation

- For recent 20 years, the world average annual number of oil spills is 21 cases/year (Kim, 2013)
- Problems (e.g. economic loss of a nation, residents and ecological damage) are occurred.
- The goals of this research are (1) evaluation of oil simulation materials that are currently available during training exercises and (2) determination of their effectiveness, advantages, disadvantages, and permitting requirements.

Requirements for the desirable oil spill stimulants

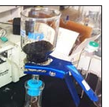
- Properties should be similar to oil and an environmentally friendly.

Material property / floating / provision / recovery /
distinguishing / not harmful to the environment

Recycle ocean wastes and Reuse as foodstuffs for aquarium animals

Fish meal as a solid simulant

- A brown powder obtained by drying the fish or fish trimmings, often after cooking, and then grinding it.
- Composed of 60~72 % of protein, 10~20 % of ash, and 5~12 % of fat (IFFO, 2011).
- Rich in a lot of EPA and DHA, which are called as omega-3 fatty acid (Cho and Kim, 2010).
- Has 2 functions; (1) solid simulants for response training and (2) growth accelerator for aquarium animals.



Fish oil as a liquid simulant

- Fishery production has been increasing from 2010.
- Except for edible parts of squid, fish guts are occupied over 20 % (Kang, 1993).
- Especially fat, vitamin B, minerals, and omega-3 are more than 40 % in squid guts (Kang, 1993).
- The problem of response training for oil spills to use fish (squid) oil is fishy smell, so this research focus on deodorization and utilization of it.

2010. (statistics)		
Rank	Type	Output
	Total	1,133,721
1	Anchovy	249,636
2	*Squid*	***159,130***
3	Mackerel	94,331
	Etc.	630,624

Development and test of oil simulants for response training

1. Experiment process for development of simulants

❖Solid simulants

Floating if over
20 % of flour

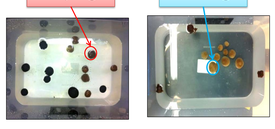
Combination percentage
Fish meal:flour=1:1
Fish meal:flour=2:1
Fish meal:flour=3:1

↓

Size
diameter 1, 2, 3cm

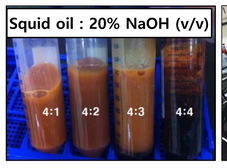
↓

Frying / Baking

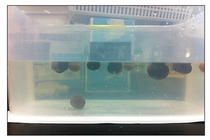
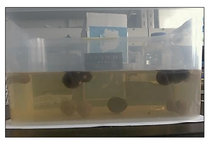


❖Liquid simulants

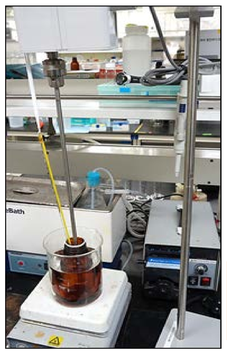
- Fish odor cause substance : free fatty acids, phosphate, and extra odor components.
- Deaciding process : removal of free fatty acids
- Utilization of Ginger, coffee grounds, charcoal, MSG.



❖Result of solid simulants: **1-2cm of fried mixture (1:1, v/v) shows best**

Fried	Immediately after start	After 2 hours (response training)	After 11 hours
Fish meal:flour = **1:1**	 Diameter 3cm settled	 3cm settled	 2, 3cm settled

❖Result of liquid simulants: **MSG shows the best for deodorization**



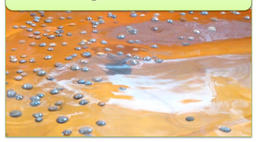
- **Principle** : Phosphate is reduced after several hours, and then peroxide value is increased, resulting in a bad smell. Water soluble protein from MSG translocate water insoluble protein of fish oil into water soluble protein in water. (Korea patent (No. 93-000779))
- **Process** : Stir a mixture(squid oil:water:MSG, weight %) at 90~100°C for 1 hour, and then leave if for 15 hours, and finally extract 80~90 % of it.

The main odor components of squid oil is **phosphate**, and **deodorization using MSG shows the best** performance.

2. Simulation test of oil simulants (5t tank)

(floating/moving/absorption/recovery)

Floating test for solid



Recovery test for solid (using a net)

Floating & moving test for liquid

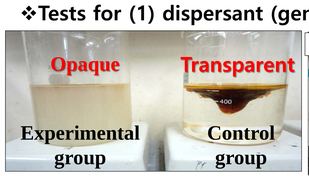
Oil skimmer operation for liquid

Recovery test for liquid (oil skimmer)

Absorption test for liquid (oil absorbent)

3. Complementary experiments

❖Tests for (1) dispersant (general SG-1000), and (2) various oil absorbents

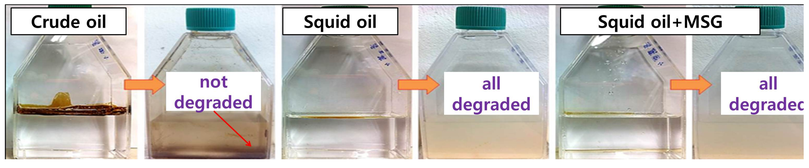


(1) Experimental group : squid oil+dispersant(20% of oil), and Control group : only squid oil. Dispersant was sprayed on squid oil with a sprayer, and stirred for 5 mins, resulting in dispersant and squid oil were reacted very well with the naked eye.
(2) The average absorption rate was almost 19.5 times of self-load.
(absorption rate = absorbent weight with squid oil (g)/original absorbent weight (g)

4. Safety evaluations

❖Biodegradation analysis

- 100mL of seawater (from west sea of Korea) with 0.1mL of squid oil was incubated at 17.5°C with 200rpm, and observed whether the squid oil was degraded by the ocean microorganisms or not. → Squid oil was totally degraded.



❖Ocean Eco-toxicological Evaluation

- Utilization of microalgae / invertebrate / larval fish for growth inhibition test and acute toxicity test.
- Based on this data, the amount of oil simulants is decided, considering about the amount of the ocean.

*NOEC : No Observation Effective Concentration
*EC/LC 50 : Concentration of being half of a population by a material

Toxicity test with the microalga (*Phaeodactylum tricornutum*)	
NOEC	3.125 ppm
EC50	20.6 ppm
Acute toxicity test with the invertebrate (*Brachionus plicatilis*)	
NOEC	3.125 ppm
LC50	33.3 ppm
Acute toxicity test with the invertebrate (*Artemia franciscana*)	
NOEC	> 100 ppm
LC50	> 100 ppm
Acute toxicity test with the larval fish (*Cyprinodon variegatus*)	
NOEC	> 50 ppm
LC50	> 50 ppm

❖Hazardous Substance Analysis

- This test is for check if simulants contain harmful materials (e.g. heavy metals, PCB) or not. As a result of all items below, all hazardous substances weren't detected or below under the standard values.

Area	Items	Acceptability
General items (12)	. Mineral oil / cyanide / phenol / chrome / zinc / copper / cadmium / mercury / organic phosphorus / arsenic / lead / nickel	*All pass*
Specific items (16)	Polychlorobiphenyl (PCB) / naphthalene / phenanthrene / anthracene / benzo[a]pyrene / fluoranthene / benzo[a]anthracene / benzo[b]fluoranthene / total polycyclic aromatic hydrocarbons(PAHs)	

5. Material property (a liquid stimulant)

Items	Results
Kinetic viscosity (40°C)	28.34 mm^2/s
Kinetic viscosity (100°C)	6.578 mm^2/s
Cleveland Open Cup (C.O.C)	228 °C
Pour Point	-7.5 °C
X-Ray sulfur analysis	0.12 mass %
Brookfield viscosity (A/2/100, 20°C)	98.4 mPa·s
Water (Karl-fishier method)	6.379 mg/kg
Specific gravity (15/4°C)	0.927
API degree	21.06

6. Field test for the final experimental simulants (Busan, in Korea)

- Product : 400 kg of solid simulants produced by EP (extruded pellet) process / 100 L of liquid simulants.
- Equipment : 9 training vessels, 60 m of oil fence, 20 kg of oil absorbents, and 2 of oil skimmers
  - Solid : a mixture of fish meal, flour, and yellow coloring / floating for 4 hours / 2 cm of diameter
  - Liquid : refined squid oil with gardenia yellow (100:1, v/v)

❖ Solid : appropriate for control training using oil fence

❖ Liquid : appropriate for control training using oil skimmer