

## **Rice husks and oil pollution**



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## Abstract

In this project, we focused on a natural product -that is the husks of rice – and its use to solve the oil pollution. The potential of rice husk for oil adsorption from aqueous solution was studied due to its special structure-skeleton of cellular structure. These properties of rice husk could be used to absorb oil. At the same time, the history and some normal methods which people always use to clean oil pollution have been introduced in the project. Under the help of our supervisor, a simple experiment has been designed in order to test the capacity of the husks of rice. Based on the experiments, we try to find whether it is possible to use the husks of rice for dealing with the oil pollution or not. At last, we gave our supposal that this method would be very useful to solve the pollution of oil, if it is able to be used in practice.

**Keywords:** oil pollution, rice husks, capacity, tetradecane, squalane

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## 1. Introduction:

Oil pollution is one of the most serious problems. And every country gets down to looking for effective methods to solve the problem. We also want to find out what way could be much better. Our aim is that we are able to solve the oil pollution while we also can make pollutant as little as possible. And we also reduce the cost as much as we can. So it is available to use the natural way. Now we prefer to choose the material of rice husk to absorb the oil pollution in the ocean. First, it is a natural way so that we could decrease the other pollution of ocean when we are getting rid of the oil pollution that caused by any man-made activities. Second, the husk of rice is very easy to be gained. Every country has farm lands in which people grow crops. Then it's cheap and easy to buy the rice husk. Third, the rate that the husk of rice absorbs the oil pollution in the ocean is very high. According to the calculation, it is as far as 73%. Have a look at the figure (table 1 ) below:

Table 1  
Overall results of the sorption tests

Sorbents	Operational time (min)	Influent oil concentration (mg <sup>l</sup> <sup>-1</sup> )	Effluent oil concentration (mg <sup>l</sup> <sup>-1</sup> )	Total oil input (mg)	Oil sorbed		
		Max; Avg.; Min	Max; Avg.; Min		Total (mg)	Per mass (mgg <sup>-1</sup> )	(%)
Kapok fiber	360	58.5; 40.9; 14.0	15.0; 6.4; 1.8	248710	206862	827	83
Cattail fiber	360	62.5; 45.3; 33.5	9.6; 5.8; 2.8	320680	277648	1107	87
<i>Salvinia</i> sp.	300	62.5; 49.3; 39.0	27.8; 7.1; 0.8	288900	236120	944	82
Polyester fiber	300	54.0; 45.3; 39.0	7.6; 2.6; 0.8	270850	253130	1008	94
Wood chip	120	61.5; 49.8; 38.0	27.2; 11.4; 5.8	116300	86020	343	74
Rice husk	120	58.0; 42.3; 27.0	15.2; 11.2; 8.2	102000	74660	298	73
Coconut husk	60	44.0; 37.6; 32.0	37.4; 24.0; 15.0	45100	14480	58	32
Bagasse	30	48.5; 40.7; 36.5	34.2; 32.7; 29.6	24400	4800	19	20

[01] [Eakalak Khan & Wanpen Virojnagud & Thunyalux Ratpukdi. Use of biomass sorbents for oil removal from gas station runoff]

Nowadays, as the scientific technique is developing fast, more social problems have appeared. And they become more and more serious. Oil pollution is one of the most important problems. Now we want to find a way of adsorbing the oil pollution. We read some article about how to solve the oil pollution before. Then we want to find out if the husk of rice is possible to absorb the oil. So we will do an experiment to test the capacity (?l oil/mg husks) of rice husks. Calculate the density of the husks of rice with oil, and then we can estimate whether it will be flow or sinking. That will be a part of our project.

**The reason why we chosen this topic because the world has been effected by the oil pollution for a long time.**

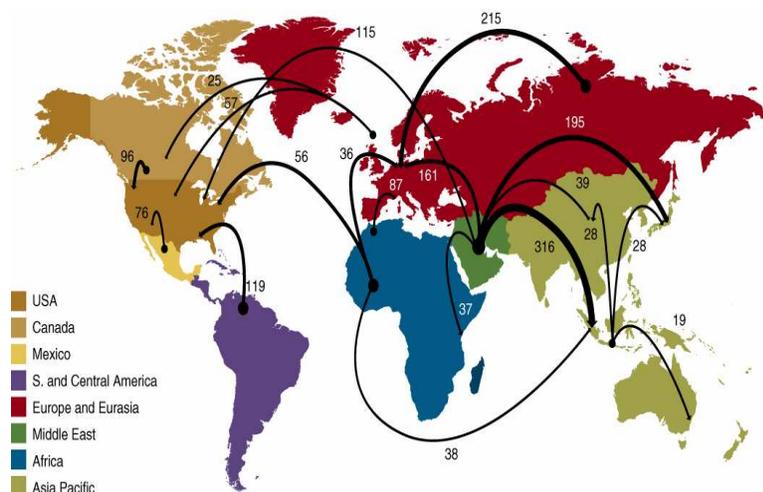
## 1.1 History of the oil pollution

Since the first oil well was discovered in 1859, the pollution has happened. It shaped with the oil discovery and exploitation. For oil crises after wars and seafaring expending; a great deal of petroleum exploitation, transportation and dispending make the oil pollution unprecedented severity.

According to statistic, every year the oil and the oil production, which are leaked into the ocean through various ways, occupy about 0.5% in the all production in the world.

Petroleum through various ways annually, the oil amount that pours into the ocean is between 10,000,000 tons and 2,000,000 tons, the pollutant of petrol amount that goes into the ocean is between 2,000,000 tons and 1,600,000 tons, among them 1/3 is the oil tankers' leak as accidents in the water.

Table2



Major oil trade routes 2003 In fact, the more oil we have traded, the more pollution we may cause.

[02] [Botkin&Keller 2005](From Environmental Science textbook by Botkin & Keller)

**T**here are about five hundred times accidents about oil pollution happened in China every year. And the quality of water nearby the sea land is 2~8 times lower than the normal mark.

Table3 history

Date	Place	Quantity of leak oil	Polluted area
1976	England	91.1 thousand liters	180 km

In March 1978	France	68 million gallons (257 million liters)	-----
1979	the east coast of Mexico	130million gallons (490 million Liters)	-----
In March 1989	in the United States (Alaska)	11 million gallons (42 million liters)	The worst oil spill
1991	Iraq deliberately released, during the Persian Gulf War	465 million gallons (13/4 billion liters)	The world's largest oil spill

## 1.2 Harm of the ocean

Oil is the water-fast compound, if oil entered into the ocean will form a big area oil-film on the ocean surface. This oil-film affects the ocean system's matter and the energy exchange.

Table4 The oil-film on the oceanic surface



As a rule, pour 1-ton oil into the ocean that will be 12 km<sup>3</sup> oil-films on the ocean surface. This oil-film prevents the oxygen from the atmosphere into the ocean, effect the ocean increase of absorbing the greenhouse gas what like CO<sub>2</sub>, increase of the greenhouse gas. Cause more global warming.

And water vapor can not evaporate to atmosphere, which conduce to the air upwards the polluted seawater area dry. The precipitation is less than other sea area.

The sea surface has the oil-film, which can increase reflectivity; reduce the solar energy into the sea water. And the oil-film also can make the oceanic temperature higher and higher, it makes the sea latent heat decrease, pollute the air, and let the sea

lose regulative competence, engender ocean-hungriness phenomena. Touch local climate and environment directly.

Pour 1L oil in sea water; it can be dissolved by 40 thousands L oxygen. So the oxygen in ocean will less and CO<sub>2</sub> will increase. As well as the sunshine also decreases into the sea, which causes a great deal algae and animalcule dead, detest oxygen biology multiply more. Ocean ecosystem food chain was broken; accordingly induce the entire ocean systemic unbalance.

Oil leak out to the offing, after a few hours, there will reaction photochemistry, product the oxide of ketone hydroxybenzene acid and sulfur. These matters disserve the ocean very serious. When the content of oil is 0.1 \_ /L in the seawater, fries mostly defectiveness. The oil pollution in the sea let the oil attach on spawn and fish's cheek, it makes a great deal of fishes die. The oil also disservices halo bios a lot; many seabirds because of oil on their wings, they can not fly or eat some fishes and shrimp that polluted by oil and they fall sick to die. Sometimes the oil pollution also affect the sea birds' ability of procreate

Ocean suffer by oil pollution in case, future trouble would persist a few years. Coastwise zoology will suffer breakage, and zoology comeback also use a few years.

[03] [<http://www.pep.com.cn/200406/ca438980.htm> (geography of High school in China)]

### **1.3 Some methods of solving the oil pollution**

Oil is made up of dissolved compounds such as C<sub>4</sub>---C<sub>17</sub>, which could form the oil film to influence commutating about matter and energy. Usually the oil film of the 1-ton petroleum on the water formation can overlay of thousand meters of squares surfaces. It is really a serious problem if oil leak in the water. The AOS of New Jersey in USA has been working for a time now. Also ERSI of USA has developing a MARINESPILL GIS system for detective the toxic matter. AVHRR of Canada (NOAA) is a man-made satellite used for watch the offing. There are hundreds of ways to solve the oil problem. Chemical way, bio way and natural way are wild used now. In

chemical way, normally use chemical compounds to neutralization with oil, bio way is used some bacteria to assimilate the oil. And the natural way (use the husk of rice to clean up the oil pollution) is the best method to choose, because of the healthy and economic. There are several normally ways solve oil pollution.

[04] [Shao Xiao Han, 'Harm of oil pollution professor of Beijing University'  
<http://www.pep.com.cn>]

#### 1. Natural dilute

Natural environment have their self-regulation, so sea can also absorb some pollution things. For example it has a big accident about an oil tanker near Spain coast in 2002. Spain government asks the other ship take it to the middle Atlantic. Ocean can dilute all the oil, which leak out of the oil tanker. But natural dilute is very limited because it have it own solubility can't dilute more things.

#### 2. Lotion decompose

We can use some lotion decompose oil. But this way is very expensive. We also need pay more attention that some lotion itself is the pollution thing.

#### 3. Deposit

Scatter the powder of calcareous to deposit oil, but it is dangerous for the animals and plants live at the bottom of the sea.

#### 4. Burn

We can burn it if the thick of oil reach to 2-3 centimeters. But this will pollute the air. The noxious gas is unhealthy for human.

#### 5. Burrier

We can use burrier fix it in a place and reclaim it if the area of oil is small.

#### 6. Absorbents

Stalks or Husks of plants we can use this things absorb oil

[05] [<http://www.pep.com.cn/dlkbbx/index.htm>.(in Chinese)(Geography of High school in China, People education press, 2003)

Our project is about this way. There are four reasons why we are interesting in this way. First is because stalks or husks are very easy and cheap to get it. The second reason is because it can really absorb more oil in the water. The third reason is because stalks

and husks of plants can float on the water. After absorbing oil, it is very easy to get it back. The last reason is because it can't pollute natural.

## 2. Problem Formulation

**Is it possible to use husks of rice in order to absorb oil?**

**What is the absorbing capacity of the husks of rice?**

## 3. Theory

Generally speaking oil pollution is caused by oil sinking. If we want to get rid of the oil from water, we can just move it away. So this is our method that we use husk of rice to absorb the oil from the polluted water. First of all, we should analyze the oil's physical and chemical properties. Oil is flammability liquid. It is a complicated kind of organic mixture. Generally it is made up of hydrocarbon compounds and a little impurity.

[03] <http://www.pep.com.cn/200406/ca438980.htm> (geography of High school in China)

Physical property: the color of oil is usually dark brown. Its density is about 0.75~0.98. The viscosity of oil can change a lot in different conditions. In normal temperature it is shaped liquid like water. And it also can assume nearly solid state.

Because it is an organic mixture, it can dissolve in litmusless organic solvent, such as benzene, chloroform, carbon disulfide, ether and so on. The freezing point and boiling point of oil depend on the content of macromolecule alkyl hydrocarbon. Anyway the physical property of oil is related with its constituent.

[06] [<http://info.datang.net/S/S1449.htm> Chinese website]

Chemical buildup: oil mostly is made up of carbon and hydrogen elements. They have taken part of 95%~99% of all. Then it also contains sulfur, nitrogen, oxygen elements and so on. As far as we know, more than 2000 compounds compose the oil. In all the compounds there are more than 230 kinds of hydrocarbon compounds, and they are

part of alkyl, cycloparaffin and aromatic hydrocarbons. And they are the basic compounds that make up of the oil.

The chemical composition of oil is made of different hydrocarbons for example alkanes. Table 5 lists different alkanes.

Table5 : List of alkanes in oil

Alkanes			
Methane CH <sub>4</sub>	Undecane C <sub>11</sub> H <sub>24</sub>	Eicosane C <sub>20</sub> H <sub>42</sub>	Nonacosane C <sub>29</sub> H <sub>60</sub>
Ethane C <sub>2</sub> H <sub>6</sub>	Dodecane C <sub>12</sub> H <sub>26</sub>	Heneicosane C <sub>21</sub> H <sub>46</sub>	Triacontane C <sub>30</sub> H <sub>62</sub>
Propane C <sub>3</sub> H <sub>8</sub>	Tridecane C <sub>13</sub> H <sub>28</sub>	Docosane C <sub>22</sub> H <sub>46</sub>	Hentriacontane C <sub>31</sub> H <sub>64</sub>
Butane C <sub>4</sub> H <sub>10</sub>	Tetradecane C <sub>14</sub> H <sub>30</sub>	Tricosane C <sub>23</sub> H <sub>48</sub>	Dotriacontane C <sub>32</sub> H <sub>66</sub>
Pentane C <sub>5</sub> H <sub>12</sub>	Pentadecane C <sub>15</sub> H <sub>32</sub>	Tetracosane C <sub>24</sub> H <sub>50</sub>	Trtriacontane C <sub>33</sub> H <sub>68</sub>
Heptane C <sub>7</sub> H <sub>16</sub>	Hexadecane C <sub>16</sub> H <sub>34</sub>	Pentacosane C <sub>25</sub> H <sub>52</sub>	Tetracontane C <sub>34</sub> H <sub>70</sub>
Octane C <sub>8</sub> H <sub>18</sub>	Heptadecane C <sub>17</sub> H <sub>36</sub>	Hexacosane C <sub>26</sub> H <sub>54</sub>	Pentatriacontane C <sub>35</sub> H <sub>72</sub>
Nonane C <sub>9</sub> H <sub>20</sub>	Octadecane C <sub>18</sub> H <sub>38</sub>	Heptacosane C <sub>27</sub> H <sub>56</sub>	Hexatriacontane C <sub>36</sub> H <sub>74</sub>
Decane C <sub>10</sub> H <sub>22</sub>	Nonadecane C <sub>19</sub> H <sub>40</sub>	Octacosane C <sub>28</sub> H <sub>58</sub>	(www.chemfinder.com)

The carbon numbers decide the quality of the compound. We choose tetradecane and squalene for the experiments. Tetradecane is one of the light oil components (low molecular weight, see keywords) and squalene is the heavy one (high molecular weight, see keywords). With a light reagent and a heavy reagent that we can know the capacity of the husks according to different oils or oil components.

### The rice husks

As we think of the rice husks can absorb the oil from water. If it is really have a good effect then we can use it to solve the oil pollution. Before we use it to solve problems we should know some details of the rice husks. We should measure the capacity to see the result and the density to know how to use it.

### Theory of adsorption

Adsorption tells you why the husks of rice can solve the oil pollution. Adsorption is the physical adherence or bonding of ions and molecules onto the surface of another molecule. It is the most common form of sorption used in cleanup. Unless it is clear which process is operative, sorption is the preferred term.

[09] [<http://www.cpeo.org/techtree/glossary/I.htm#ion>]

### Gas chromatography-Mass spectrometry (GCMS)

GCMS is an abbreviation for Gas chromatography-Mass spectrometry, an advanced piece of chemical analytical equipment typically used to characterize complex organic mixtures.

Table6 This is GCMS (gas chromatography mass spectroscopy).

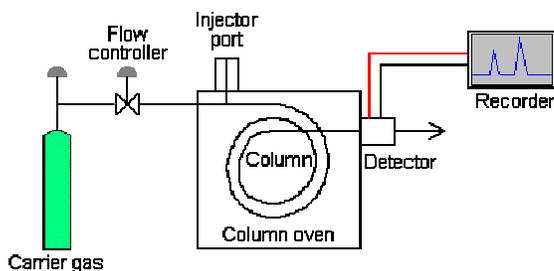


[10][<http://www.gmu.edu/departments/SRIF/tutorial/gcd/gc-ms2.htm>]

Gas chromatography - specifically gas-liquid chromatography - involves a sample being vaporized and injected onto the head of the chromatographic column. The sample is transported through the column by the flow of inert, gaseous mobile phase. The column itself contains a liquid stationary phase which is adsorbed onto the surface of an inert solid.

Have a look at this schematic diagram of a gas chromatograph:

Table7 GCMS



[11][<http://www.shu.ac.uk/schools/sci/chem/tutorials/chrom/gaschr.htm>]

[12][IAN A. FOWLIS 1995. 'Gas Chromatography' Page 152, Fig.6.5.a. HRGC/MS combination]

### B. GCMS measurement

**GCMS** is an abbreviation for Gas chromatography-Mass spectrometry, an advanced piece of chemical analytical equipment typically used to characterise complex organic

mixtures.

The **gas chromatography** stage separates the mixture into its various constituent parts (i.e. substrate and series of active compounds) which are then then passed off to the mass spectrometer for individual characterization

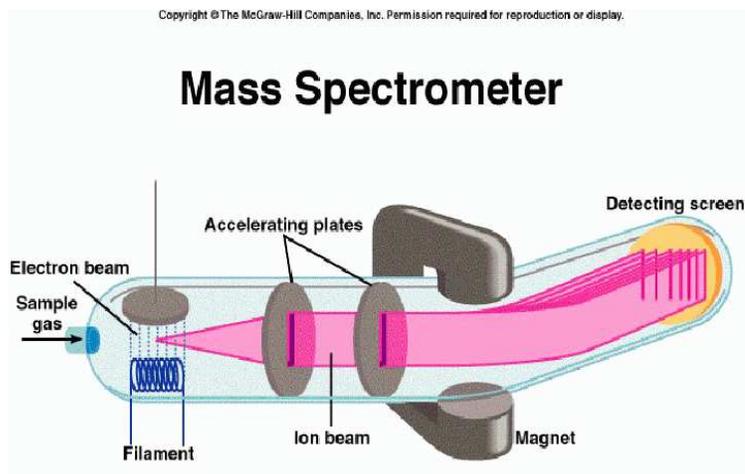
[13]<http://www.abbreviationz.com/>, Copyright 2005 STANDS4 LLC

It is used to test the compounds and get the molecular weight so we can know the name of compounds.. How does it run?

First we need to put the matter into a glass vial and the machine can run it. Then when we put the vial into the machine and the machine will run by a robot arm. Only the gas can go into the machine, so the matter will become gas by the temperature. And the gas will go with helium into a glass channel about 15 metres. Normally the temperature is from 100 degree to 300 degree. Each second the temperature will be include of 25 degree so it will be higher quickly. We set up the time for 3 minutes at the beginning. Naphthalene will comes out at 6.45, tetradecane will comes out at 7.35 and squalane will comes out at 15.41.

**Mass spectrometer** is like a detector. With this part we can know the molecular weight of the compounds. First the sample gas comes into the filament and from electrons become to ions. Then the ions cross the magnet to detect part. The result will be shown at detecting screen and we could know it. Because of we know the molecular weight of the compounds now.

Table 8 Mass spectrometer



[14] Picture from: [copyright ? The McGraw-Hill Companies, Inc. Permission required for reproduction or display.]

(The picture shows the Mass spectrometer run. The gas comes into filament part and cross the magnet field then will show the result by detecting screen.)

Our samples will run as the description before. Then we put the results together with standard to compare to see the results.

## 4. Methodology

As we think of the rice husks can absorb the oil from water. If it really has a good effect, we can use it to solve the oil pollution. Before we use it to solve the problems, we should know some details of the rice husks. We should measure the capacity to see the result and the density in order to use it.

Procedure:

### Part A. Density

We need to know if the rice husk will float or sink when they absorb the oil. We use pure water and sea water to test it.

First use a glass cup with pure water (10ml) and put 1g rice husks inside. We add 0,1g of oil (tetradecane) into the water, mix them well and wait for 3 to 5 minutes. Write down the result by percentage of floating husks.

The same test is made in saltwater. The saltwater is made by adding 0.3g salt into 10ml pure water and then mix them well.

### Part B. Capacity

We try to do some experiments to test the capacity. The amount of oil adsorbed by the husks (the capacity) is measured by putting husks of rice into water with a known amount of oil in it. After adsorption of the oil, we extract the oil from the husk of rice using an organic solvent. We make samples and compare with an internal standard (naphthalene) then we can compare our results.

1. We make the standard first. The standard uses tetradecane and dichloromethane. We use a syringe to move 100ul of tetradecane into 10ml dichloromethane (DCM) and mix them as well as possible. Then dilute it to 1:100 in DCM. At last we add 10ul (0.5g/ml) naphthalene as an internal standard. Move some mixture into a vial and close the top.
2. We need three samples. Each sample use 0.1 gram rice husks. Wash the rice husks first with clean water, use a glass stick shake them well and waiting the dust drop down. Then get them out with a glass funnel.
3. Put 100ul tetradecane into 10ml water and mix well. Add the rice husks into the mixture and shake well. Wait 3-5 minutes then use a glass funnel to collect the husks. Use clean 100 ml water to wash the husks 3-5 times put them into another funnel to transfer them into a separation tract.
4. Now the husks are extracted in the separationtract. Add 10ml dichloromethane into the funnel and shake 3-4 times. (Don't forget open the valve to set out the gas!). Then use a glass bottle named 'Sample 1' to catch the first extraction. (Don't forget to take off the top of the funnel!).
5. Add 2 x 10 ml of dichloromethane again for extract 2 and extract 3. Wash a syringe (100ul) with DCM for 35-50 times to get rid of the tetradecane, and waiting for use at mark 6.
6. Dilution of the extracts. REMEMBER to add the internal standard to each samples, this is done by adding 10ul internal standard, 10ml DCM and 100ul of the extract into a new bottle. In this way the samples has been diluted 100 times and are ready for analysis. Note that extract 3 has not been diluted, and the

internal standard has been added directly into the 10 ml extract. The samples are transferred to gcms-vials for analysis on gcms.

\*The second time we use the sea water for the experiment. Put 5g NaCl in to 200ml water and the concentration is 2.5%.

## 1. Purpose of experiment

To test how much oil the rice husks can absorb. If the capacity of rice husks is high, it can be used as a way to solve oil pollution. We choose two typical compounds in oil. Test the rate that the solvent contains compounds.

## 2. Reagent and appliance

### 2.1 Sorbents

Rice husk is the sorbents tested. The fresh rice husk samples should be washed with tap water to remove impurities outwardly. Then all the samples are dried at normal temperature.

All the samples are used without sieving, because in practice we needed not to sieve the large amounts of sorbents.

### 2.2 Oil

Because this test is considered a bench scale test, we replace oil into tetradecane and squalene. The main reason is that tetradecane and squalene is alike of oil in some important chemical and physical characters. For oil is made up of compounds of alkanes as the table above, and oil does not have changeless constitutes, choosing tetradecane and squalene in place of oil is OK.

### 2.3 Solvent

As the characters, tetradecane and squalene cannot be dissolved into the water, and can be dissolved into the organic solvents. We choose the  $\text{CH}_2\text{Cl}_2$  as the solvent. It can dissolve tetradecane and squalene from water well.

Table 9 chemical compounds

Name	MolecularFormula	FormulaWeight	CASNumber	Bp	Density
Tetradecane	$\text{CH}_3(\text{CH}_2)_{12}\text{CH}_3$	198.39	629-59-4	252-243 degree	0.763g/ml at 25 degree
Dichloromethane	$\text{CH}_2\text{Cl}_2$	84.93	75-09-2	39.8-40 degree mmHg	1.325g/ml at 25 degree
Squalane	$[(\text{CH}_3)_2\text{CH}(\text{CH}_2)_7\text{CH}(\text{CH}_3)(\text{CH}_2)_7\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2]_2$	422.81	111-01-3	176 degree/0.05 mmHg	0.81g/ml at 25 degree
Naphthalene	$\text{C}_{10}\text{H}_8$	128.17	91-20-3	218 degree	— — — —

[15][ 'Handbook of Fine Chemicals and Laboratory Equipment' Aldrich, 2003-2004]

## 2.4 Appliance

All the appliances should be cleaned with distilled water and dried in oven.

We used:

a. Top-loader balance, sensitivity, +/- 0.001g

(Top-loader balance,)

b. Some weighing papers

c. 100µl glass syringes (100µl = 0.1ml)

(We use two kinds of 100µl glass syringes. the below one is filled by  $\text{C}_{14}\text{H}_{30}$ .)

d. 10ml graduated cylinders

e. Beakers (50ml and 100ml)

f. Battles

g. Vials, caps

h. labels

i. stirring rods

j. separatory funnel

## 3. Operation

### 3.1 Experimental setup

We wanted to do three series of experiments to test the capability of rice husks' sorption. In every series, we weighed 0.1 gram rice husks. With the same mass, results could be easy to compare between series.

We do three series experiments, and every series we called a group.

In the first group, we put 100 microlitre tetradecane and 100 microlitre squalene into the water, and then add the rice husks in it. In the second group, we put 200 microlitre tetradecane and 200 microlitre squalene into the water, and in the third group we put 400 microlitre tetradecane and 400 microlitre squalene into the water.

After the rice husks absorbed the tetradecane and squalene in the water, washed the rice husks and put into the solvent of  $\text{CH}_2\text{Cl}_2$ . Then the tetradecane and squalene is dissolved into the  $\text{CH}_2\text{Cl}_2$  from the rice husks. Measure the capacitance of tetradecane and squalene in the  $\text{CH}_2\text{Cl}_2$ , we will know how much oil rice husks can absorb.

### 3.2 Process of experiments

#### i. Preparation

- a. Clean all the appliances with distilled water and dry.
- b. The 100 $\mu\text{l}$  glass syringes is filled with  $\text{CH}_2\text{Cl}_2$  and put off 50 times to clean the 100 $\mu\text{l}$  glass syringes before every time we used it.
- c. Weighed rice husks

Weighed the weighing paper first, zeroed, then weighed about 0.1g rice husks, repeated the processes above twice to make three samples of 1g rice husks.

#### ii. Experiment

- a. Make the standard

Used the 10ml-graduated cylinder to measure 10ml  $\text{CH}_2\text{Cl}_2$ . And we used a 100 $\mu\text{l}$  glass syringe to measure 100 $\mu\text{l}$  tetradecane and 100 $\mu\text{l}$  squalene, shaking. When the tetradecane and squalene dissolved in  $\text{CH}_2\text{Cl}_2$  the almost, put the solution into a bottle. Then filled a 100 $\mu\text{l}$  glass syringe with the solution from the bottle, put it into the 10ml  $\text{CH}_2\text{Cl}_2$  (this process means to dilute the solution 100 times), shaking. It is the sample of standard.

Put it into a vial, enveloped with cap, marked a label as 'S'.

- b. Make the samples of tests

The first group of samples

We cleaned the rice husks with distilled water for 3 times, in the meanwhile, measured

10ml water and 100µl tetradecane and 100µl squalene, put the 100µl tetradecane and 100µl squalene into the water.

We put the 10ml water with 100µl tetradecane and 100µl squalene into the 50ml beaker. Put the 0.1g rice husks in it, churned up with stirring rod. Then we dipped the rice husks in it for 5 minutes.

After 5 minutes, with the medicine dropper, we moved aside the redundant tetradecane and squalene on the water (because the tetradecane( $C_{14}H_{30}$ )'s density is lighter than water and can not be dissolved into water).

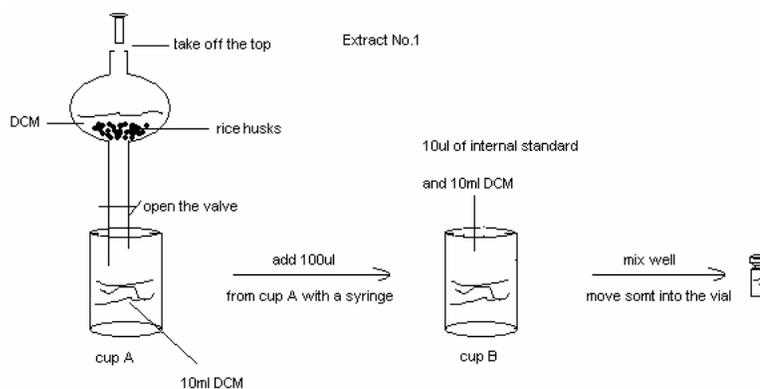
We washed the rice husks with distilled water three times to remove the tetradecane and squalene, which clung on it. Then we swilled the liquid, and put the rice husks in the separatory funnel, also added the 10ml  $CH_2Cl_2$  in funnel, shaking adequately.

Then only put the solution from the funnel into a bottle, but left the husks in the separatory funnel. We marked the bottle as '1.1'.

After that, we put the 10ml  $CH_2Cl_2$  in the separatory funnel again, shaking. And put into a bottle marked '1.2'.

Then, we put the 10ml  $CH_2Cl_2$  in the separatory funnel the third time, shaking. And put into a bottle marked '1.3'.

Table 10 Extract No.1



(The three samples and the separatory funnel)

Because the solution in bottle 1.1 has big consistency, we filled a 100 $\mu$ l glass syringe with the solution from the bottle 1.1, and put it into the 10ml CH<sub>2</sub>Cl<sub>2</sub> (this process means to dilute the solution 100 times), shaking.

(Filled a 100 $\mu$ l glass syringe with the solution from the bottle 1.1)

We put it into a vial, enveloped with cap and marked 1.1. We put the solution from 1.2 and 1.3 to the vials separately, and named them 1.2 and 1.3.

So that is sample 1.1, sample 1.2, and sample 1.3 of group 1.

We did the same processes to make the group 2 and group 3. The differences are that we added 200 $\mu$ l tetradecane and 200 $\mu$ l squalene in the group 2 and 400 $\mu$ l tetradecane and 400 $\mu$ l squalene in the group 3.

In the end of the tests, we got three groups of samples (1.1, 1.2, 1.3; 2.1, 2.2, 2.3; 3.1, 3.2, 3.3.) and a sample of standard.

We put all samples and standard in the **GCMS** to get the final results.

#### 4. Analysis and improving

Because this experiment is operated exploringly. So the exactness is unknown, and we should analysis each experiment's results and improve it.

We have done this experiment three times, and every time we have some improves.

To understand why we changed the processes to improve the experiment, the first thing should be known is experimental forecast.

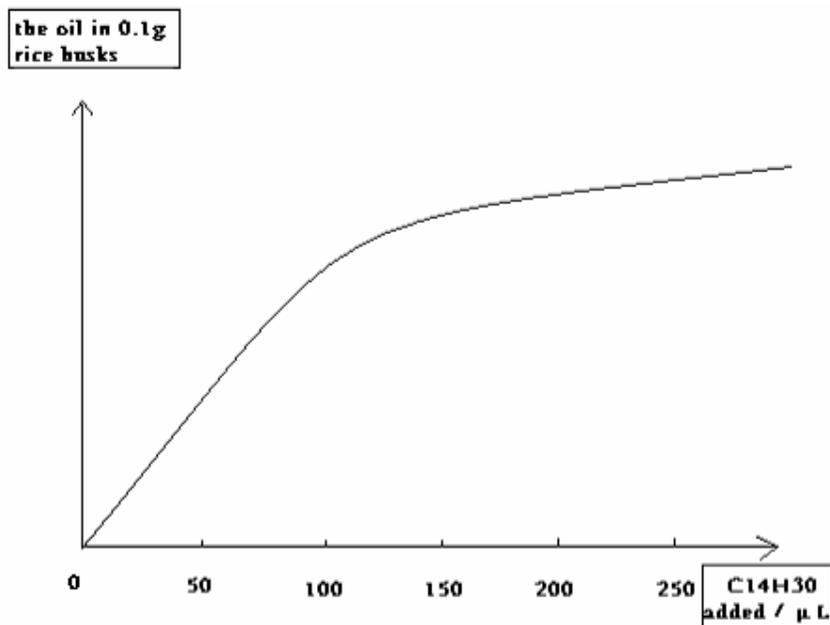
## 4.1 experimental forecast

We did three groups in one experiment and three tests in one group. Add the standard, we got ten data as results, named 's', '1.1', '1.2', '1.3', '2.1', '2.2', '2.3', '3.1', '3.2', '3.3'. 's' is a result as maximal capacity that oil (tetradecane and squalene in the experiment) is absorbed.

Take the '1.1', '1.2', '1.3', '2.1', '2.2', '2.3', '3.1', '3.2', '3.3' into three parts, the first part is '1.1', '2.1', '3.1', which is the solution after washing the rice husks in the separatory funnel the first time in each group. The second part is '1.2', '2.2', '3.2', which is the solution after washing the rice husks the second time in each group. The third part is '1.3', '2.3', '3.3', which is the solution after washing the rice husks the third time in each group. So there are contrasts between three tests in a part.

Make part 1 as an example, we expected we can the result below:

Table11 diagram



Look at this graph, it is the perfect result we wanted to get. There, we have two expectations, the first one is to prove that there is some oil (in the experiment tetradecane and squalene take place of oil), and the second one is to prove that the more oil added (in the experiment we added tetradecane and squalene in place of oil), the more the rice husks can absorbed. But it is not a direct ratio. In fact, with the

tetradecane and squalene added, the oil (tetradecane and squalene in experiment) in rice husks increase fast in the beginning, and then increase slowly, in the end, it even no increase.

## 4.2 Analysis and improving

### 4.2.1 Analysis in the first time and improving in the second time

The first time we do the experiment all the same as the Process of experiments, we added tetradecane and squalene as 100µl, 200µl, 400µl. Then the result has been analyze, we found out that the tetradecane in the rice husks increase unclearly from 100µl to 400µl. That means the increase is slow. And in the first time, we added the squalene to take place of the heavy part of oil, but in the result the squalene did not appear in the rice husks, so that means the rice husks can not absorb the heavy part of the oil.

For this analysis above, we change the tetradecane from 100µl, 200µl, 400µl into 50µl, 100µl, 200µl, and we canceled the squalene which is added, as the heavy part of oil, because the rice husks are not effective to the squalene, heavy part of oil.

### 4.2.2 Analysis in the second time and improving in the third time

The second time we went to the lab to do the experiment we had changed. Then we analyze the result, we found out that the tetradecane in the rice husks increase so fast from 50µl to 200µl. That is a clear result, but we have some difficulty to compare the results among 50µl, 100µl, 200µl, for the increase is so large.

For this analysis above, the third time we do the experiment, we add the 100µl additive in the all samples of texts (all samples of texts = '1.1', '2.1', '3.1', '1.2', '2.2', '3.2', '1.3', '2.3', '3.3'). The additive is made up of CH<sub>2</sub>Cl<sub>2</sub> and 2-Methylnaphthalene as a measure. Because it has a fixed content in every samples, and all the content of tetradecane in rice husks can compare with it, to confirm the tetradecane in the rice husks in each sample more or less.

Then, we will get the result of experiment.

### 4.2.3 Analysis in the third time and improving in the forth time

Because we do the experiment to know how much the rice husk can absorb the oil in the sea. To be close to the fact, we improved our experiment third time.

- a. In fact the rice husks absorb the oil in sea water, so this time we change the boiled water into salt water. We put NaCl 3 gram into the 200 ml water and shaking, when added oil in it.
- b. Actually we use rice husk clean the oil in sea, the oil pollution must serious and the oil is much in the sea water. So the forth time we added 100µl 200µl, 400µl oil again to close with practice.
- c. If we use the rice husks to absorb oil in the sea, how we reclaim the rice husks is a big problem. There two case may happen, the one is the rice husks with oil can float on the sea. In this case, we just have to filtrate the sea water above and reclaim the rice husks. The other case is that the rice husks with oil sink in the sea, it hard to reclaim, so we should look for some methods else, for example, take them in nets when the rice husks are put into water. Then we just reclaim the nets, and the rice husks will be reclaimed.

Thus, we should find if the rice husks could sink or not when they absorbed the oil.

## 5. Results and discussion

Tetradecane:

1. Standard with Sample 1 of Tetradecane

$$\text{Capacity} = \frac{M_{\text{Tetradecane in husks}}}{M_{\text{Tetradecane in standard solvent}}}$$

$M_{\text{Tetradecane in husks}}$  : mass of tetradecane in the husks

$M_{\text{Tetradecane in standard solvent}}$ : mass of tetradecane in the standard solvent

Capacity: the capacity of absorbing tetradecane compared with that of standard solvent

Because the intensity of Dichlomatine in GC-MS is so stable that Dichlomatine can be

the reference. So, the ratio of intensity of Tetradecane and Dichlomatine can substitute the mass of Tetradecane in Dichlomatine. That is where,

**Capacity = Ratio of Tetradecane in husks and Dichlomatine /**

**Ratio of Tetradecane in starndard solvent and Dichlomatine**

Thefefore,

$$\text{Standard} = 42257693 / 22642842 = 1.866$$

$$\text{Ext1} = 1334797 / 20306714 = 0.0657$$

$$\text{Ext1} / \text{Sta} = 0.0657 / 1.866 = 0.0352 = 3.52\%$$

The capacity of sample 1 is 3.52%.

For the concentration of 100myl tetradecane, the capacity is very low. From 3.52% to 0.461%. For 400myl group the capacity is acceptable, from 40.6% to 0.37%. And it shows us is can be used to solve the oil pollution.

Table 12 Calculate ratio of Tetradecane

Name	Ext1	Ext2	Ext3
Sp1(100myl)	3.52%	0.767%	0.461%
Sp2(400myl)	40.6%	0.37%	--
Sp3(400 myl)*	648%	14.9%	4.3%

\*No internal standard

(Look at the no internal standard group, the result of the 648% is a strange result, because it is too large. It may because of the mistake of dilute. May be this group is not diluted so well.)

Data from Tetradecane

Table 13 results of Tetradecane

Name	Retention Time	Area	Area%	Ratio%
Standard	6.444	22642842	34.889	58.583
	7.249	42257693	65.111	100.00
Sample 1	6.446	20306714	93.832	100.00
	7.256	1334797	6.168	6.573
Sample 2	6.443	23214063	40.596	68.338
	7.249	33969371	59.404	100.00
Sample 3	6.442	21262002	53.765	100.00
	7.248	18283985	46.235	85.994
Sample 1 (400 myl)	6.444	18532324	24.804	32.985
	7.256	56183779	75.196	100.00
Sample 2 (400 myl)	6.444	22401923	26.716	36.456
	7.254	61448831	73.284	100.00

\*Standard is used for all the samples.

From sample 1 to sample 3 is used 100myl tetradecane and the left samples are used in 400myl tetradecane. The first line of the result is dichlomatine and the secone line is tetradecane. Sample 1 is diluted for 100 times in both 100myl and 400myl groups. The standard worked with nephatalene as a internal nephatelane. (with the retention time of 6.444 seconds). The internal standard is used for test the GCMS system for get the good results. With a internal standard we can see if it is so stable in the machine and the result won't changed by the GCMS system.

### Squalane

It can use Squalane/Standard of Squalane \* 100% , and will get the result.

(For all 400myl group the result should divide by 4, because of the standard is for 100myl group.)

Table 14 Calculate ratio of Squalane (without internal standard)

Name	Ext1	Ext2	Ext3
Sp1(100myl)	3.626%	0.346%	0.035%
Sp2(400myl)	7.51%	0.302%	--

The capacity of 100myl group is from 3.626% to 0.035%, almost the same with the 100myl group of tetradecane. And the capacity of the second group in 400myl is from 7.51% to 0.302%. It can absorb some squalane here.

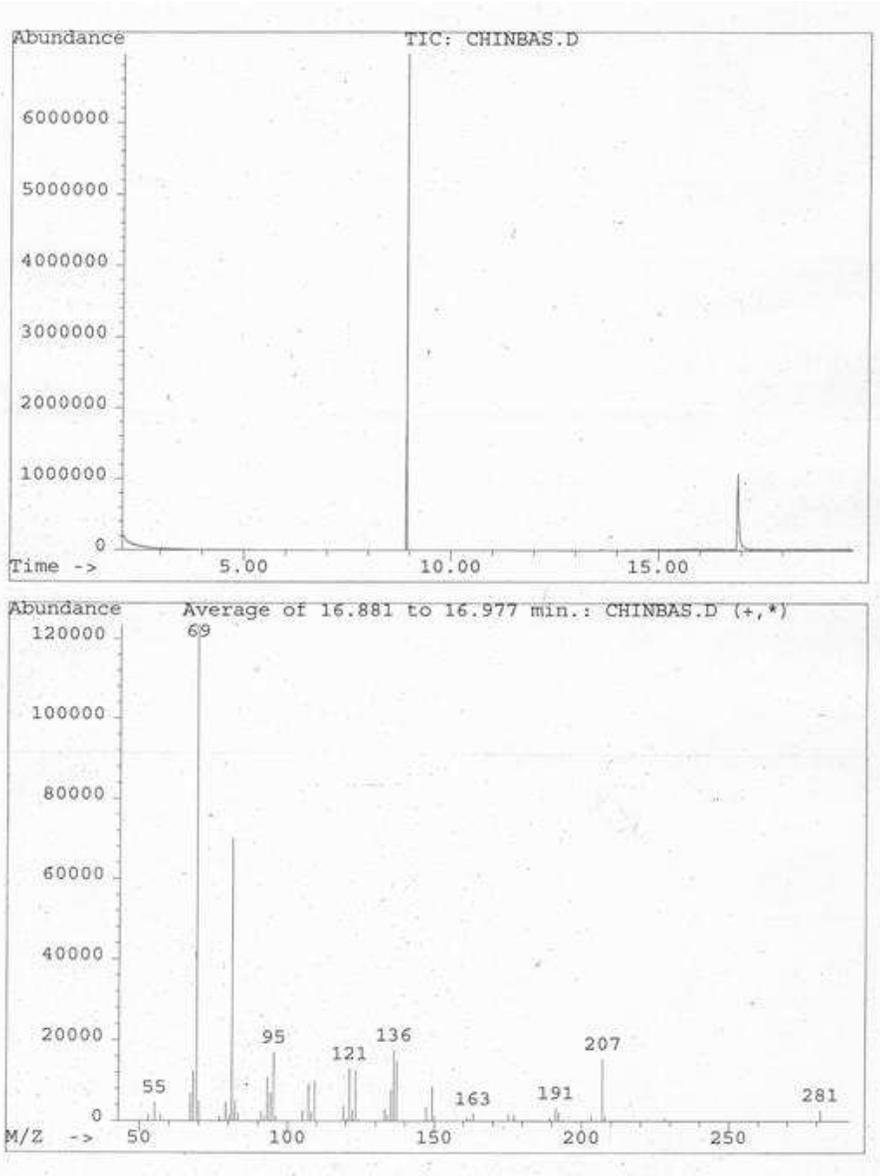
## Data from Squalane

Table 15 results of Squalane

Name	Ret. Time	Area	Area%	Ratio %
Standard	7.257	195008	21.561	27.487
	15.407	7096850	78.439	100.00
Sample1	15.405	257305	100.000	100.000
Sample2	15.425	245578	100.000	100.000
Sample3	15.406	245533	100.000	100.000
Sample1*	15.405	213295	100.000	100.000
Sample2*	15.410	85553	100.000	100.000

\*Standard and sample 1 to 3 is worked with 100myl Squalane. Sample 1\* and 2\* worked with 400myl Squalane. Only the standard and sample 3 without diluted for 100 times. The squalane experiments without a internal standard.

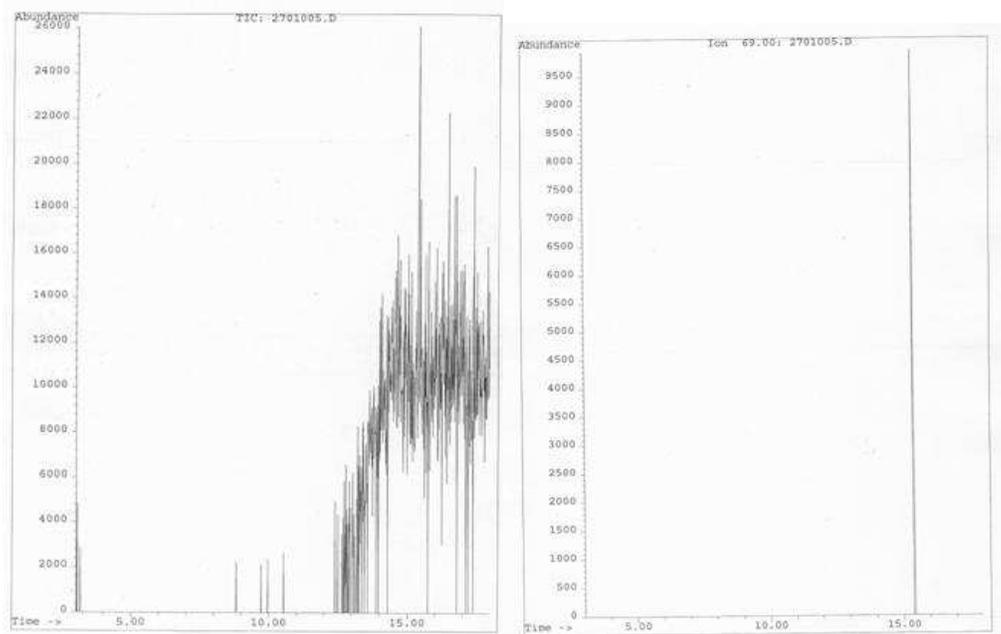
Table16 result from squalane



A fragmentation pattern of squalane we see, that the ion mass 69 has the highest abundance in the mass spectrum.

From the first part of the table we can see two lines. They have the same concentration but with the different measurement. What has happened with the short one? It is because of the squalane at that temperature is not so stable, and become to some other things. So there are lots of noises here. And we can not see it clearly. And with choose a abundance ion mass the result will be much more readable.

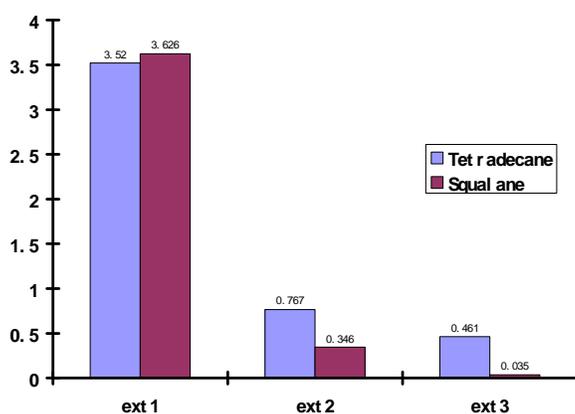
Table17 result from squalane(mass spectrum) Table18 the result with choose the ion mass 69 of squalane



As we have known the squalane becomes some other thing at that tempatrue. To the left table, the sum of the output for all masses in the range 50-500 g/mole – to the left, and can not see the result with so much noise. So we choose the isolated output for just the mass 69 g/mole – the noise reduction is very clear. (The right table)

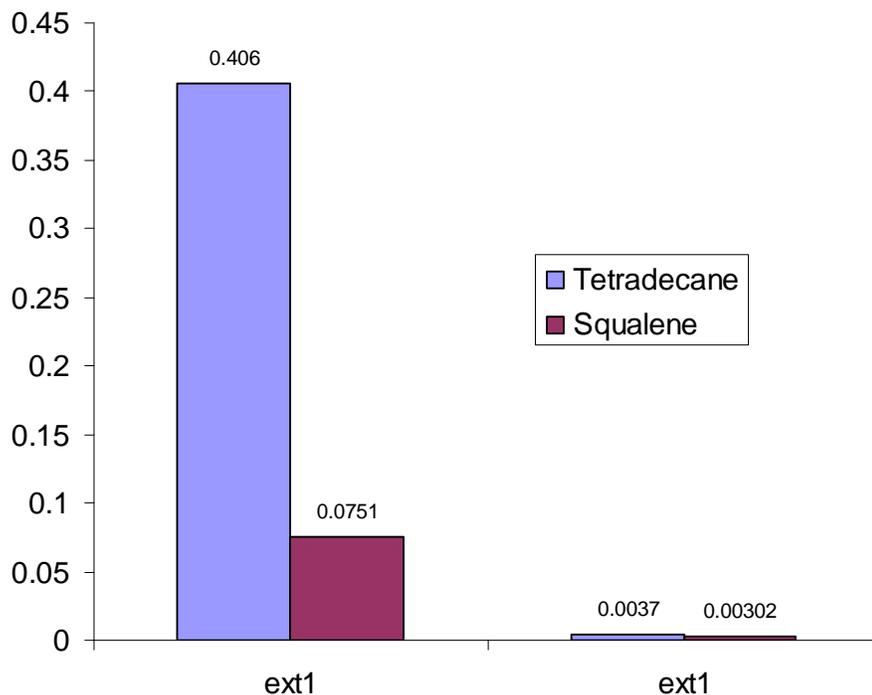
Table 21 are diagrams of tetradecane and squalane. Though they are quite different chemical compounds but we found the capacity of them are almost the same (the numbers are almost superimposed images).

Table 21 Diagram 100myl



In 400myl group (table 22), we found the capacity of tetradecane and squalane are not the same. It has a large change here, not as the group with 100myl before. So the capacity of a high concentration is different.

Table 22 Diagram of 400myl



Look at the results, we found the rice husks are good for use when the concentration is high. And with the result the capacity become higher when the concentration became higher both of tetradecane and squalane---the light oil and the heavy oil. But with a low concentration it can not absorb some of them.

So the rice husk can be used for solve the critical oil pollution. For the small area pollution with low concentration oil pollution maybe to burn it away is the best. And when the rich husks has absorbed the oil can be collected, also for burn to get energy and heat.

### **Conclusion:**

The capacity of adsorption for the husk of rice is about 5% in most cases. For the

lighter parts of the oil (tetrdecane) the adsorption is higher, when the load of oil is increased. For the heavier parts of the oil (squalane) the adsorption was constant – about 5 % - independent of the start concentration of oil in water. In both of fresh water, 55 % of the husks were sinking, while the rest was on the experiments, and in the salt water is about 70%.

### **Perspective:**

Now we have finished our experiment. This is just a simple experiment. Through the data from the experiment we can see that the husk of rice is a feasible way to absorb the oil pollution in the ocean. So we are sure that we can put it into practice. Then we will do more experiments about this project. It is the beginning of the whole project experiment. We have already made the plan for the coming experiment. Later we will try more organic materials that maybe are the coconut husk, wood pieces and bagasse, because the materials have their special properties. The result which we use them to absorb the oil pollution would be different. And we just try the husk of rice in a surrounding that is in the normal condition. So we should try more times in other conditions, such as acidic, alkaline and so on. That is our work in the future. Moreover, we can't lose sight of the phenomena of the absorbed rice husks. When the husks of rice have absorbed the oil, there maybe are two phenomena. One is that the absorbed rice husks floats on the sea. And the other is that the absorbed rice husks sink into the water. If they are floating on the sea, it will be very easy to collect them. We can just use a net to enclose them together. However, if they will sink into the water, it will be more difficult to gather and collect them. So we should think more to solve this problem. Then make a system in order not to produce extra pollution. We must consider these two results. The cost of the two results is pretty different. The words above are about the following experiment. Then we talk some about the expectation that is how to deal with the absorbed rice husks. As the husk of rice cannot absorb all the oil, there is some oil remained. But it can be got rid of by the oceanic circle system. Perhaps we can mix some other materials together to absorb the oil. In that case, the

result should be perfect. Then the absorbed rice husks which we have collected can be used for the second time. One is that we can burn it directly to get heat or energy that can be used for production. Second, the country could set a company to use the absorbed rice husks for industry as oil raw material. Through this viewpoint, we can see the husk of rice is a double win way as the method of solving the oil pollution.

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