REGENERATION STUDY OF SPENT NICKEL CATALYST BY USING MICROWAVE TECHNIQUE IN OLEOCHEMICAL INDUSTRY

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***Abstract*— Regeneration of spent catalyst is a method to revive the function of the spent catalyst same as fresh catalyst. In this research, regeneration technique is achieved by using microwave trough existence of oxygen. The objectives this study is to compare the characteristics between fresh and spent Nickel catalyst, and to study the regeneration of Nickel catalyst using microwaves technique. Microwave technique was used with existing of oxygen gas set at 1 L/min through all the experiment. The parameter that is investigated was power (300W, and 600W) and time (30 mins, and 60 mins). Characteristic of the fresh, spent and regenerated Nickel catalyst was investigated in term of its surface area and porosity distribution by using BET, BJH, Horvath-Kawazoe, Dubinin-Radushkevich and Dubinin-Astakhov. Also thermal characteristics using Thermal Gravimetric Analysis (TGA) and X-Ray Diffraction (XRD)**

I. INTRODUCTION

Catalyst is a chemical that added into a process to increase rate of reaction of process. In hydrogenation process of oleochemical industry, catalyst is used to increase rate of reaction for the hydrogen molecule added into double bond of long chain fatty acid. Also, the choice of catalyst to use for hydrogenation greatly affects the properties of the final product (Balakos and Hernandez 1997). Stearic acid is one of the example for long chain fatty acid that have 18 carbon-hydrogen bond. The application of hydrogenation process of long chain fatty acids is to convert unsaturated to saturated fatty acid by breaking the C=C double bong into C-C single bong. Hydrogenated fatty acid has huge advantages that it is more stable than unsaturated fats (Mozaffarian, Jacobson, and Greenstein 2010). In this study, Nickel catalyst was used for hydrogenation process of fatty acid to form a saturated fatty acid from unsaturated fatty acid. After repeated uses, nickel catalyst has high possibly to be contaminated by residual fats and oils, insoluble acids, support materials and filter aids. Thus, the catalyst would become less active and lose the catalytic functions that end as "spent catalyst". Due to the presence of organic or inorganic residues, spent catalysts are classified as hazardous wastes which potentially pose a harmful effect on the environment and human health that requires compliance with stringent environmental regulations. Also the cost and demand of nickel has been rising significantly (Oza,R. and Patel 2012).

As a result of the stringent environmental regulations on spent catalyst handling and disposal, research on the development of process for recycling and reutilization of waste hydrotreating catalysts has received considerable attention. Studies review base on research (Marafi and Stanislaus 2008), various options such as: *(a) minimizing spent catalyst waste generation,(b) utilization to produce new catalyst sand other useful materials, (c) recycling through recovery of metals and (e) treatment of spent catalysts for safe disposal, are available for refiners to handle the spent catalyst problem.*

However in this paper only focus on two available options to reduce the solid waste of catalyst which is reducing the catalyst consumption or regeneration of catalyst and reuse. Reducing usage of catalyst seams not a good way because it may affect reaction rate and productivity. Regeneration of spend catalyst is the best way to reduce solid waste because useful life of catalyst can be extended. There have been a study to regenerate metal catalyst using Microwave method but it was for petrochemical industries. This technology makes it possible to recover and reuse platinum (Pt) catalyst waste and reduce the negative environmental impact of the disposal of spent catalysts in petrochemical industry (Jou and Lo 2017). However, there is no yet a study about regeneration of metal catalyst using Microwave for oleochemical industry. Thus, this study will continue to focus for oleochemical industry. Purpose of this study is to study and compare the characteristics of regenerated and fresh Nickel catalyst and to study the regeneration of Nickel catalyst using microwaves technique.

II. METHODOLOGY

A. Materials

The main material used is fresh and spent Nickel Catalyst get from Emery Oleochemical Sdn Bhd. Nickel catalyst MONCAT 1991 used in the hydrogenation process of stearic acid. Sample of spent nickel catalyst was taken from Niagara Filter section after the hydrogenation reaction. It is collected in spent Nickel catalyst collection drum. Feed and product stearic acid sample was used in this study because the Nickel catalyst was used for hydrogenation of stearic acid at period.

B. Characteristics.

Table 1: Summary of characterization analysis

Characteristics	***Study area***	***Method***
Physical properties	Surface area and pore size	BET
	Thermal characteristics	DSC – TGA analysis
Chemical properties	Elemental composition	XRF analysis
	Functional Group	FT-IR

C. Experiment

Domestic modified microwave is used with maximum power of 1000M. Quartz reactor used in the experiment is connected with gas tubing from gas tank. Oxygen gas is used and the flowrate is regulated using a regulator. The experiment is carried out by measuring 100g of the spent Nickel catalyst and pour into beaker. The beaker was then put inside the Quartz reactor. Flowrate of oxygen gas was maintained at 1 L/min through the experiment. Oxygen gas was let flow into the reactor as a purging process to fully occupied oxygen gas inside the reactor. The power of microwave is set at 300W and 600W with time 30 minutes and 60 minutes for each set of power.

III. RESULTS AND DISCUSSION

A. Fourier-transform infrared (FTiR) spectroscopy Analysis

Stearic Acid

The result of absorption and transmission of the spectrum create a molecular fingerprint of the sample (Nicolet and All 2001). The fingerprint is the identified as a specific information about the vibration and rotation of the chemical bonding and molecular structures, making it useful for analyzing organic materials and certain inorganic materials. Stearic acid is a long chain fatty acid under functional group of carboxylic acid of organic material. It have 18 number of carbon chain (C-C) and have composition of 5.2% in palm oil (Montoya et al. 2014). The IR spectroscopy wave of carboxylic acid is under range of 3300-2500 cm^{-1} and the conjugation of fatty acid showed it strong signal for unsaturated fats under the range of 1710-1685 cm^{-1}. Based on the graph of Figure 1, it show peak of 2914.81 cm^{-1} which is strong and broad stretching of O-H and 1697.69 cm^{-1} of C=O bond for conjugation of fatty acid (LibreTexts 2014). Asymmetric bending vibrations of -C-H are observed at 1450 cm^{-1}, which is near the scissoring band in the spectra of hydrocarbons occurring at 1463.83 cm^{-1} (Kadamne et al. 2009). In addition, peak of 934.01 cm^{-1} and 726.87 cm^{-1} shows trans-cis formation of fatty acids. Also, the are medium bending of O-H bond on peak 1430.09 and 1411.05 cm^{-1} which falls into the range of 1440-1395 cm^{-1}.

For the stearic acid product from hydrogenation process, the wavenumber are approximately almost the same for the carboxylic acid functional group. Consist of strong and broad stretching of O-H bond at wavelength 2915.76 cm^{-1}. This may due to existence of unsaturated of fatty acid in saturated product because it is impossible for process has conversion of 100%. Thus, the reading if FT-IR for product stearic acid is same.

Spent Nickel catalyst

FTIR analysis is important for spent Nickel catalyst in order to know the existent of stearic acid adsorbed on the catalyst surface after hydrogenation process. From figure 3, the highest peak is at wavelength 2915.23 cm-1. These show that there is existent of stearic acid at the catalyst surface because carboxylic acid is under range of 3300-2500 cm-1. There is no clear sign of saturated or unsaturated but what important is sign of carboxylic bond. This result justify that all oil need to be removed for regeneration process. Also state that Nickel catalyst has the capability to adsorb liquid substance may because of porous characteristics itself. This part will discuss letter on the surface area and porosity distribution analysis section.

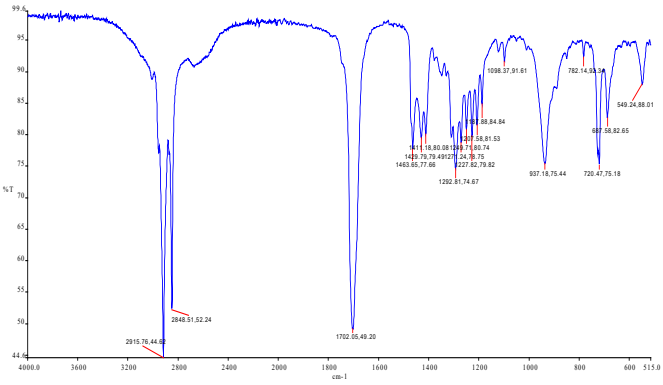


Figure 1: Feed steric acid of hydrogenation process

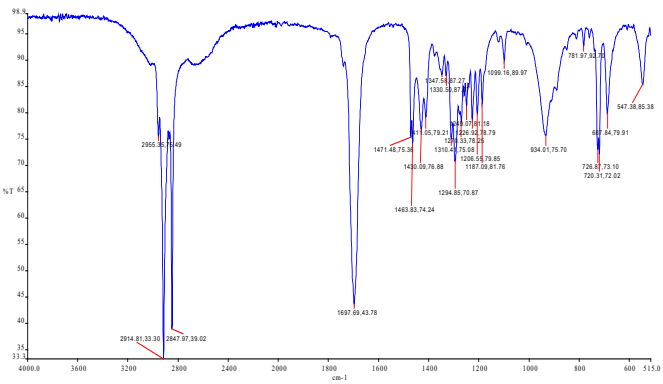


Figure 1: Product stearic acid of hydrogenation process

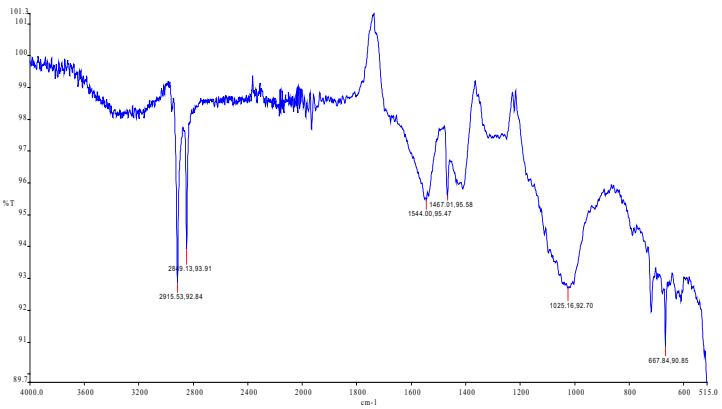


Figure 2: FTIR analysis of spent Nickel catalyst

B. Thermal gravimetric Analysis

Weight loss and thermal behavior of nickel catalyst used in hydrogenation of stearic acid were investigated by means of TGA and DCS. The analysis was set at heating rate 10 °C/min and maximum temperature 1000 °C. Table 1 show fresh Nickel catalyst only has two stage of decomposition at temperature from 179.52 °C to 399.59 °C. Meanwhile, there are 2 stages for spent Nickel catalyst and the first step of decomposition are usually considered as moisture content because the regions from room temperature to 300 °C were ascribed to desorption of physisorbed and chemisorbed water as describe in literature (Burattin, Che, and Louis 2002). There is possibility that the Nickel catalyst is silica supported catalyst. Because based on X-Ray Fluorescence (XRF) analysis for fresh catalyst it consist 1.047% of silica.

For first stage of fresh Nickel catalyst, there is no moisture contend because it start decomposed at high temperature 179.52 °C, water start to evaporate at 100 °C Weight loss of the catalyst sample above 300 °C could be due to slow decompositions of nickelphyllosilicate in the catalyst sample leading to the formation of nickel oxide. Hence, calcinations process of the dried sample above 300 °C would generate nickel oxide that was evenly dispersed in the catalyst. Metal oxide dispersed in calcined catalyst could generate coarse or large metal particles after reduction process as reported in the literatures.

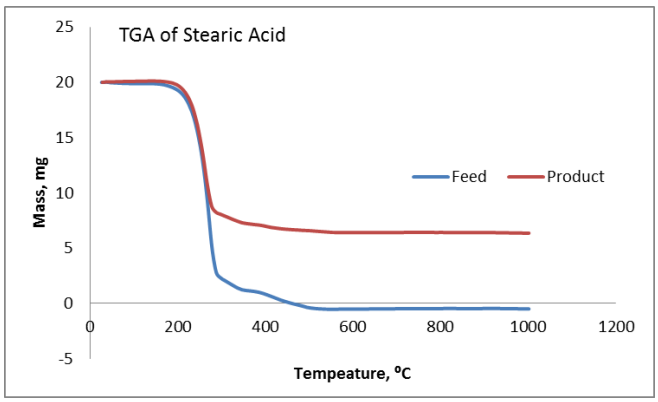
The second step decomposition of fresh Nickel catalyst show the decomposition of stearic acid between 394.75 – 433.902 °C and for spent between temperatures 242.89 – 446.72 °C. From these result, it is relatable for the decomposition temperature of stearic acid based on Table 1 both for feed and product stearic acid. Stearic acid fully decomposed to form carbon only substances at 356.36°C. Fortunately, based on TGA/DSC analysis there was no sintering of Nickel where it occur where it may occur at temperature 900 – 1300 °C (Saitou 2006). But during the hydrogenation process, the was pure Nickel metal formed at 600W 60min. This say that microwave have tendency to produced very high temperature condition more than 1300 °C. Thus, based on the observation suggests that it is better to have temperature control for regeneration process to avoid metal sintering because it may affect the quality of catalyst. Sintering of Nickel catalyst may reduce its catalytic behavior and require other additional method of regeneration to recover the functionality of Nickel catalyst in hydrogenation process of stearic acid.

Table 2: TGA analysis between feed and product stearic acid

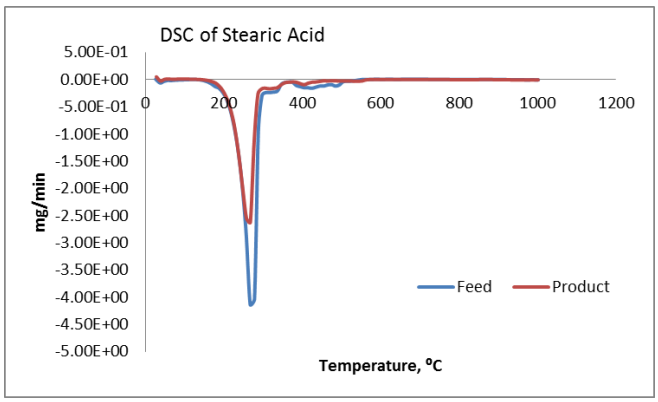
Feed Stearic Acid		***Product Stearic Acid***	
Sample weight, mg	20	Sample weight, mg	20
Residue, mg	1.1853	Residue, mg	7.2357
Moisture content, %	-	Moisture content, %	-
Temperature range, °C	139.96 - 355.54	Degraded Temperature, °C	120.83 - 356.36

Table 3: TGA analysis between fresh and spent Nickel catalyst

Fresh Nickel Catalyst		***Spent Nickel Catalyst***	
First step (1st)		**First step (1st)**	
Sample weight, mg	20	Sample weight, mg	20
Residue, mg	6.7495	Residue, mg	17.1669
Moisture content, %	0	Moisture content, %	2.8358
Temperature range, °C	179.52 – 399.59	Degraded Temperature, °C	27.41 – 143.85
Second step (2nd)		**Second step (2nd)**	
Sample weight, mg	6.7495	Sample weight, mg	19.0891
Residue, mg	5.2828	Residue, mg	16.4829
Moisture content, %	-	Moisture content, %	-
Temperature range, °C	394.75 – 433.90	Temperature range, °C	242.89 – 446.72

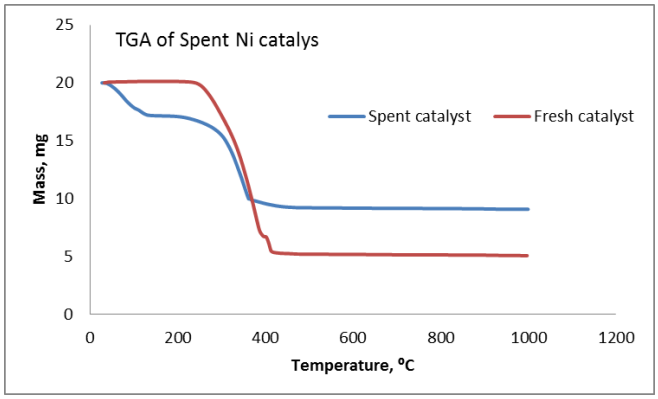


(a)

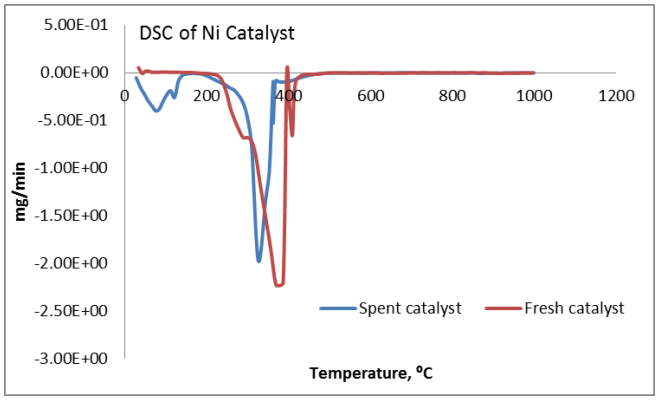


(b)

Figure 4: TGA/DSC analysis for feed and product stearic acid from hydrogenation process



(a)



(b)

Figure 5: TGA/DSC analysis for fresh and spent Nickel catalyst

C. Mass different of microwave regeneration process

Regeneration start with setup of power 300W for 15, 30 and 60 minutes. For this power setup, the highest mass different is at 60 minutes where 47.5g of substances including oil being removed from the sample. The lowest is at 15 minutes where 17.9 of substances being removed. Furthermore, after 300W power of 600W is being setup with same period of regeneration for 15, 30 and 60 minutes. The result are same as 300W where the longer period of regeneration give higher mass different. The highest is at 60 minutes where 69g of substances are being removed. In addition, at 600W 60 minutes, the result show that there is possibility for pure Nickel is being formed. Silver coloured of solid is formed, this might be that the supporter or carrier for the catalyst might mostly being removed during the regeneration process due to extreme temperature and power.

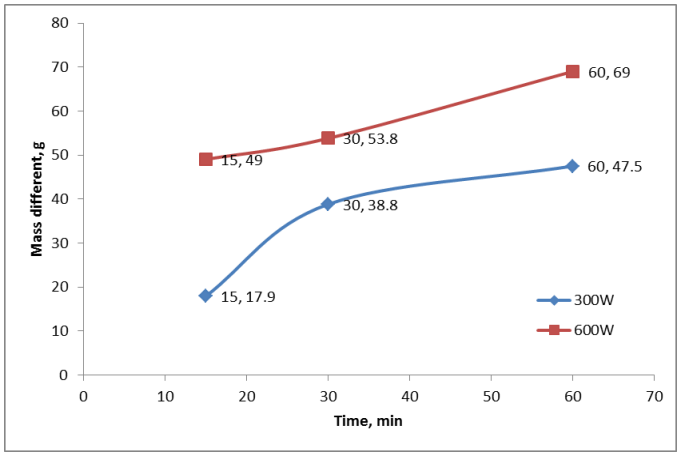


Figure 6: Result of mass different against time of the regeneration process

Table 4: Mass different of the regenerated spent Nickel catalyst

D. Surface area and porosity distribution

Table 4: Surface area and porosity distribution of Nickel Catalyst

Parameter	***Surface area ($m^2 g^{-1}$)***	***Pore volume ($cm^3 g^{-1}$)***	***Average pore width (A)***
Fresh Nickel Catalyst			
Single-point surface area at p/p^o = 0.077757477	0.2346		
Single-point adsorption P_v ($cm^3 g^{-1}$) (less than 1,934.646 A width at p/p^o = 0.99)		0.006954	
Single-point desorption P_v ($cm^3 g^{-1}$) (less than 1,934.646 A width at p/p^o = 0.99)		0.007814	
BET surface area	0.006954		
Adsorption average pore diameter (4V/A by BET)			186.7702
Desorption average pore diameter (4V/A by BET)			209.8677
Langmuir surface area	9.2460		
t-plot external surface area	2.1054		
BJH adsorption (between 8.162A and 3000A width)	1.799	0.007891	175.493
BJH desorption (between 10.197A and 3000A width)	6.1612	0.008021	52.072
D-H adsorption (between 10A and 3000A width)	1.936		155.537
D-H desorption (between 10A and 3000A width)	6.3339		53.560
Spent Nickel Catalyst			
Single-point surface area at p/p^o = 0.077757477	0.3074		

BET surface area	0.6466		
Langmuir surface area	1.7303		
t-plot external surface area	1.3575		
BJH adsorption (between 8.162A and 3000A width)	0.829	0.000504	24.331
BJH desorption (between 10.197A and 3000A width)	0.8394	0.001211	57.722
D-H adsorption (between 10A and 3000A width)	1.169		25.358
D-H desorption (between 10A and 3000A width)	0.9244		59.081
300 W			
a) 30 minutes			
Single-point surface area at p/p^o = 0.077757477	0.5043		
Single-point adsorption P_v (cm^3 g^{-1})		0.002304	
(less than 1,934.646 A width at p/p^o = 0.99)			
Single-point desorption P_v (cm^3 g^{-1})		0.002367	
(less than 1,934.646 A width at p/p^o = 0.99)			
BET surface area	2.1564		
Adsorption average pore diameter (4V/A by BET)			42.7343
Desorption average pore diameter (4V/A by BET)			43.9109
Langmuir Surface Area	5.2622		
t-Plot external surface area	2.7518		
Horvath-Kawazoe		0.002505	
(Maximum pore volume at p/p° =0.9942)			
Dubinin-Radushkevich Micropore	1.9251		
Dubinin-Astakhov Micropore	0.7813		
b) 60 minutes			
Single-point surface area at p/p^o = 0.077757477	15.6353		
Single-point adsorption P_v (cm^3 g^{-1})	0.072037		
(less than 1,934.646 A width at p/p^o = 0.99)			
Single-point desorption P_v (cm^3 g^{-1})	0.075003		
(less than 1,934.646 A width at p/p^o = 0.99)			
BET surface area	21.4951		
Adsorption average pore diameter (4V/A by BET)			134.0531
Desorption average pore diameter (4V/A by BET)			139.5721
Langmuir Surface Area	37.6033		
t-Plot external surface area	29.2208		
Horvath-Kawazoe		0.075335	
(Maximum pore volume at p/p° =0.993)			
Dubinin-Radushkevich Micropore	27.6198		
Dubinin-Astakhov Micropore	19.6348		
600W			
a) 30 minutes			
Single-point surface area at p/p^o = 0.077757477	62.3069		
Single-point adsorption P_v (cm^3 g^{-1})		0.167140	
(less than 1,934.646 A width at p/p^o = 0.99)			
Single-point desorption P_v (cm^3 g^{-1})		0.174581	
(less than 1,934.646 A width at p/p^o = 0.99)			
BET surface area	69.5374		
Adsorption average pore diameter (4V/A by BET)			96.1440
Desorption average pore diameter (4V/A by BET)			100.4242
Langmuir Surface Area	115.2741		
t-Plot external surface area	70.8497		
Horvath-Kawazoe		0.174953	
(Maximum pore volume at p/p° =0.9929)			
Dubinin-Radushkevich Micropore	87.0783		
Dubinin-Astakhov Micropore	73.4736		
b) 60 minutes			
Single-point surface area at p/p^o =	0.021367		
Single-point adsorption P_v (cm^3 g^{-1})		0.021162	
(less than 1,934.646 A width at p/p^o = 0.99)			
Single-point desorption P_v (cm^3 g^{-1})		0.021367	
(less than 1,934.646 A width at p/p^o = 0.99)			

BET surface area	7.1944		
Adsorption average pore diameter (4V/A by BET)			117.6552
Desorption average pore diameter (4V/A by BET)			118.7958
Langmuir Surface Area	11.2193		
t-Plot external surface area	7.2228		
BJH adsorption (between 10A and 3000A width)	7.642	0.021927	114.775
BJH desorption (between 10A and 3000A width)	7.4096	0.021837	117.885
D-H adsorption (between 0.090A and 3000A width)	8.720		100.516
D-H desorption (between 10A and 3000A width)	7.1688		119.971

Surface area and porosity is an important attribute to the catalytic behavior of the catalyst. The masopore, macropore or micropore of the catalyst particle really effect the behavior of the reaction as it create a pathways for rapid diffusion and improve the reaction kinetics (Takahashi et al. 2005). Spent Nickel catalyst was taken from oleochemical industry of hydrogenation process of stearic acid. The spent Nickel catalyst then regenerate using microwave technique and test it surface area and porosity characteristic using Brunauer-Emmett-Teller (BET) equipment. From the result of analysis BET surface area is obtained at standard temperature and pressure (STP). Fresh Nickel catalyst have the lowest BET surface area which is 0.006954 m^2 g^{-1} compare to spent nickel catalyst 0.6466 m^2 g^{-1} which is spent Nickel catalyst is higher than the fresh catalyst. The mesopore surface area studied through BJH adsorption/desorption surface area, the single point surface area and volume, and DH adsorption/desorption surface area. However, not all sample have BJH and DH surface area like sample 300W (30 minutes, 60 minutes) and 600W (30 minutes). This show that the sample does not have mesopore. Instead, the sample have micropore which identify by Horvath-Kawazoe pore volume, Dubinin-Radushkevich surface area and Dubinin-Astakhov surface area.

The functionality of the Nickel catalyst in hydrogenation process really depends on the porosity. Interaction between pore size and length with molecule size of the stearic acid is the main aspect to consider for Nickel catalyst effectiveness as stated in literature (Coenen 1986). Bases on the literature, pore size distributions and cumulative surface areas is important for accessibility of stearic acid molecule that effect on the effective diffusion coefficient, which appears to drop from the bulk value to zero in the range of pore widths between 35 and 15 A.

During regeneration process of 600W 60min, pure Nickel is assumed to formed. This says that Common to all types of Ni/SiO2 catalysts is that silica is not an inert support material. The silica, used for catalyst preparation, undergoes drastic structural changes as a result of a strong chemical interaction between nickel compounds and silica. Always, some basic nickel silicate, nickel antigorite, is formed, and this has an important function as a sintering inhibitor for the nickel metal and as bonding compound to anchor the nickel crystallites to the support.

In principle, the activity per unit mass of nickel seems to be proportional to the nickel surface area, so that fat hydrogenation can be considered as a structure-insensitive reaction. In many cases, however, this proportionality is not apparent, because part of the nickel surface area is insufficiently accessible for the large fat molecules. To accommodate the large nickel surface on a silica particle, which at the same time must have sufficiently large particles to be filtered from the oil after use that have been used in Emery Oleochemical industry. They use Niagara Filter to filter spent Nickel catalyst. The particle must have an extensive pore network and a large internal surface area. This porous structure must satisfy specific criteria. Nickel surface in pores of 2 nm or less is not accessible and does not contribute to activity. Active surface, in pores wider than about 3.5 nm, is fully accessible and gives fast and selective hydrogenation. In the intermediate range of pore widths the reacting molecules can still penetrate, but due to mass transport problems, selectivity is impaired (Coenen 1986).

IV. CONCLUSION

Microwave regeneration technique for recovery of spent Nickel catalyst is effective at power 300W 30min because the surface area compared to fresh catalyst is closest than other sample and there are high possibility that pure Nickel may formed from 600W 60min setup. Pure Nickel formed because of sintering that the microwave have a tendency to produce high temperature condition higher than 1300 ^{o}C. Because of that, it suggested that further technique may require before it is able to apply in the process. For example chelating or bleaching may require follow by mixing with fresh support material which is silica. Microwave technique provide deep penetration through the catalyst particle, thus this method is very cost effective that it is does not required much energy compare to conventional catalyst.

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