



## **Synthesis of Mesoporous Silica Using Gelatin as a Template and Cr/silica Catalyst For Hydrocracking of Waste Lubricant Oil**

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**Abstract :** Extraction of gelatin from bovine bonewas carried outusing a combined method of acids and bases. The gelatin was extracted from the bone using a solution of 4% acetic acid for 3, 6, and 9 days, 0.1 M sodium hydroxide for 24 h and 1.0 M hydrochloric acid for 1 h. The gelatin was characterized by electrophoresis and infra red (FTIR). The mesoporous silica (SM) was synthesized by adding a solution of TEOS as silica source into the gelatin solution and stirred for 24 h. The formed gel solution was filled intoan autoclave and hydrothermally treated at 100 °C for 24 h. The products was then calcined at 550 °C for 5 h. The silica was characterized by FTIR, x-ray diffraction (XRD), transmission electron microscope (TEM), gas sorption analysis (GSA) and acidity test. The silica wasthen poured into a solution of Cr salt precursor ( $\text{Cr}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ) for 24 h, thendried and reduced with  $\text{H}_2$  gas to obtain Cr/SM catalyst. The Cr/SM catalystwas characterized by scanning electron microscope (SEM-EDS), GSA and acidity test as well as the activity test in the hydrocracking of waste lubricant oil. The weight ratio of lubricant/catalystwas25, 50, and 75 wt. %. The liquid product of hydrocracking was analyzed by gas chromatograph-mass spectroscopy (GC-MS).The results showed that the gelatin consisted of  $\alpha$  chain collagen in weight distributionof 83-182 kDa. Thesilica shown a wormhole-like pore with avarage diameter of 3.42 nm, specific surface area of 279.06  $\text{m}^2/\text{g}$ , and pore volume of 0.46  $\text{cm}^3/\text{g}$ . The Cr/SM catalyst has pore diameter, specific surface area, pore volume of 3.41 nm, 233.77  $\text{m}^2/\text{g}$  and 0.42  $\text{cm}^3/\text{g}$ , respectively. The hydrocrancking of lubricant in a lubricant/catalyst ratio of 75produced highest liquid products of 37.12 wt.%with selectivity for gasoline and diesel oil fraction was 13.73and16.90 wt.%.

**Keywords:** gelatin, mesoporous-silica, hydrocracking, waste lubricant.

### **Introduction**

The fact from Agency of Indonesia Statistics mention that in 2007 the number of vehicles in Indonesia reached 54.8 million and increased to 104.2 million vehicles in 2013, this means that there has been increasing number of vehicles to reach 90% within 5 years. The increase of this vehicles number has resulted in increasing the number of lubricant oil as part from maintenance and repair to maintain the stability of the vehicle performance.

Regeneration of waste lubricant oil to reduce the impact of environmental pollution is a difficult thing. One of the most effective ways is the hydrocracking of lubricant oil into fuel by using a specific catalyst<sup>1-5</sup>. The  $\text{ZnO}/\text{Nb}_2\text{O}_4$ -ZAAH catalyst has been used in hydrocracking of lubricant oil that produced gasoline and diesel fraction of 38.87 and 14.10 wt.%<sup>3</sup>. Hydrocracking of lubricant oil also had been carried out with zeolite-Y and

ZnO<sup>4</sup>. The Cr-ZAA catalyst with a catalyst/lubricant ratio of 2/3 (w/w) produced gasoline fraction of 56.70 wt.% obtained from hydrocracking of waste lubricant<sup>5</sup>. The catalysts used in the previous works were loaded into a microporous supports<sup>1-15</sup>. The microporous materials could not accommodate a big molecule with high molecular weight such as heavy oil residue, waste organic and inorganic that potential as a source of oil. Mesoporous material is an alternative to be developed as catalyst support.

Research on Mesoporous materials are already highly developed in various applications for adsorbent<sup>16</sup>, catalysts and/or catalyst supports<sup>17-20</sup> such as carbon<sup>18,21</sup>, MCM-41<sup>13,16</sup> and mesopore silica<sup>17,19-23</sup>. One important factor in the synthesis of mesoporous material is the selection of template. Mesoporous silica had been successfully synthesized using gelatin extracted from cow bone as a template<sup>24-26</sup>. This silica have not been further evaluated in spite of the fact that this mesoporous material is potential to be used as a catalyst support.

To develop the utilization of the silica as a catalyst support, research work of impregnation of synthesis of mesoporous silica and Cr metal supported onto the mesoporous silica for hydrocracking of waste lubricant oil was evaluated. The results were discussed in the following section.

## Experiments

### a) Materials and reagents

Bovine bone from Yogyakarta market, analytical grade of HCl, NaOH, TEOS (tetraethylorthosilicate), Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, glacial acetic acid was purchased by E. Merck (Germany).

### b) Extraction and characterization of gelatin

The extraction of gelatin from bovine bone is previously pretreated in acetic acid 4% solution in variations of 3, 6 and 9 days. After filtered and dried, the sample was then pretreated with NaOH 0.1 M 24 h and 1.0 M HCl for 1 h, followed by hydrolysis process using aquabides for 5 h at temperature of 70 °C, filtered and dried in an oven. The gelatin was then analyzed by FTIR (Shimadzu Prestige-21) and sodium dodecyl sulphate-polyacrylamide gel electrophoresis (SDS-PAGE, Mini Protein II Bio-Rad Laboratories Inc., Richmond, CSA, USA).

### c) Synthesis and characterization of mesopore silica (SM).

The synthesis of mesoporous silica was carried out by adding a solution of TEOS as silica source into the gelatin solution and stirred for 24 h at 100 °C. Mesoporous silica was then calcined at 550 °C for 5 h. Furthermore, mesoporous silica before and after calcination were characterized by FTIR (Shimadzu Prestige-21), XRD (XRD-600 Shimadzu), TEM (JEOL JEM-1400), and Surface Area Analyzer (Quantachrome NovaWin version 11.0).

### d) Synthesis and characterization of Cr/SM catalyst

The silica sample was poured into a Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O solution while stirring for 24 h, filtered, then dried in an oven at 100 °C, calcined in nitrogen gas at 500 °C for 5 h followed by reduced with H<sub>2</sub> gas at 400 °C for 5 h produced Cr/SM catalyst. The Cr/SM catalyst was characterized by acidity test using ammonia as an adsorbed base vapor and SEM-EDS (JEOL JED-2300).

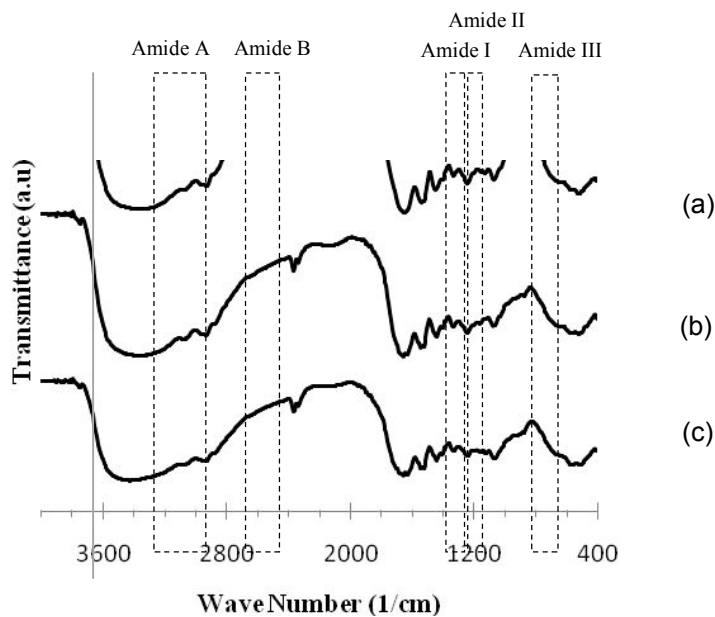
### e) Catalyst activity test

The activity of Cr/SM catalyst was tested in hydrocracking of waste lubricant in variation of lubricant/catalyst weight ratio of 75, 50, and 25. The hydrocracking process was carried out at 450 °C for 2.5 h under H<sub>2</sub> gas flow (10 cc/min.). The liquid products obtained were analyzed by GC-MS (Shimadzu QP2010S).

## Results and Discussion

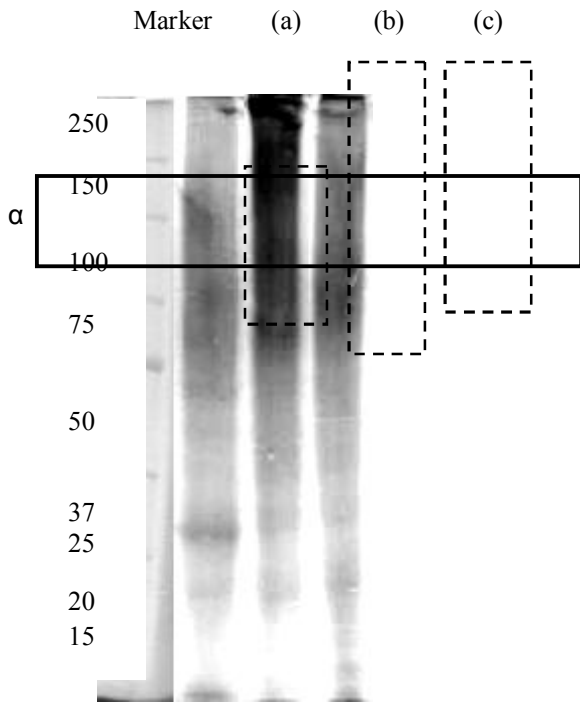
### Effect of acetic acid pretreatment towards characteristics of gelatin

Figure 1 indicated the 5 regions of amide group which is typical of gelatin, ie amide A, amide B, amide I, amide II and amide III. Amide A appears at wave number of about 3600-3400  $\text{cm}^{-1}$  for the stretching vibration of NH and OH groups. Amide B appears at wave number of about 3000-2800  $\text{cm}^{-1}$  which is stretching vibration of  $\text{CH}_2$ . Amide I appears at wave number of about 1700-1600  $\text{cm}^{-1}$ , which shows the C=O stretching vibration and bending vibration of NH. Amide II appears at wave number 1575-1480  $\text{cm}^{-1}$  which shows the NH bending vibration and CN stretching vibration. Amide III appears at wave number of 1240-670  $\text{cm}^{-1}$ , which shows the combination of the CN stretching vibration and deformation of the NH amide linkage and absorption arising from vibration wagging  $\text{CH}_2$  functional group of the side chain of glycine and proline.



**Figure 1 FTIR spectra of bovine bone gelatin with pretreated of acetic acid for (a) 3 days, (b) 6 days, and (c) 9 days**

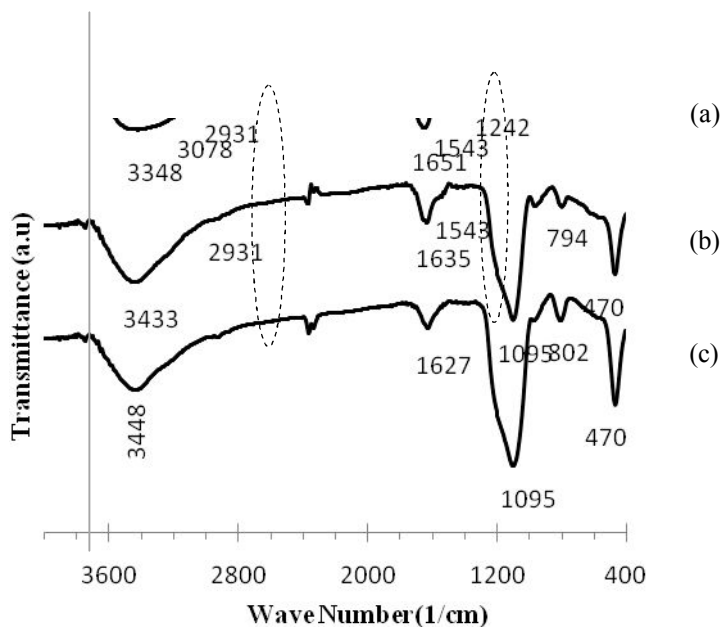
The SDS-PAGE data informed that gelatin extracted with acetic acid for 3 days has a molecular weight distribution between 83-182 kDa that narrowest compared to those of the 6 and 9 days treatments. This result suggested that components of the gelatin treated in 3 days was not as complex as the result of gelatin treated with acetic acid for 6 and 9 days. Gelatin with a molecular weight distribution between 120-160 kDa that show dominance collagen  $\alpha$  chain can be used as templates in the synthesis of mesoporous silica because the gelatin has many functional group of amino ( $\text{NH}_2$ ) which will interact strongly with silanol ( $\text{Si-OH}$ ) on the species silicate through hydrogen bonds to form a mesoporous silica material<sup>23</sup>.



**Figure 2** Profile of SDS-PAGE of bovine bone gelatin with pretreated of acetic acid for (a) 3 days, (b) 6 days, and (c) 9 days

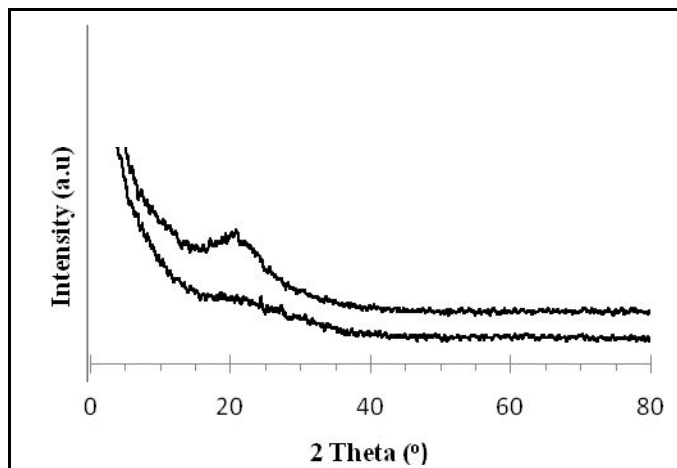
**Characters of mesoporous silica (SM) and Cr/SM catalyst**

Formation of mesoporous silica framework using gelatin as a template showed the occurrence of hydrogen bonds between amino functional group (NH<sub>2</sub>) and silanol group (Si-OH) in the gelatin was described in Figure 3..



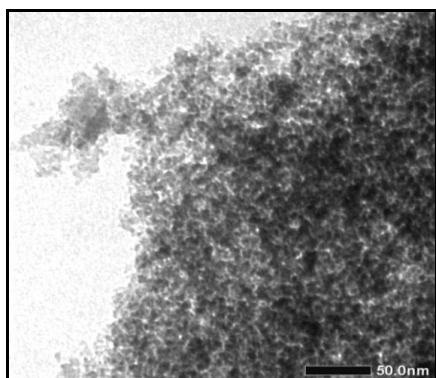
**Figure 3** FTIR spectra of (a) bovine bone gelatin, and mesoporous silica: (b) before and (c) after calcination

Figure 3 showed the FTIR spectra of sharp absorption peak at wave number of  $3433\text{ cm}^{-1}$  indicating stretching vibration of the OH groups from silanol (Si-OH) that binds to the NH stretching vibration of a gelatin template. The absorption peak at  $2931$  and  $1543\text{ cm}^{-1}$  which is characteristic absorption of gelatin was disappeared after calcination (Figure 3 (c)). This phenomenon indicates that the calcination process has been effectively eliminate the gelatin template.



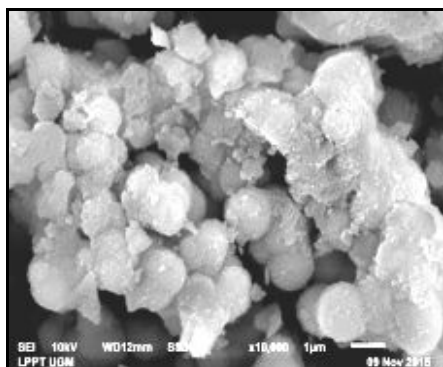
**Figure 4 Diffractograms of mesoporous silica synthesized (a) before and (b) after calcination**

Figure 4 showed that the SM was an amorphous material. In large angle of XRD diffraction, the framework of mesoporous silica material can be observed at an angle of about  $20^{\circ}$ . After calcination there is a wide peak around  $21^{\circ}$  angles shown that the framework of mesoporous silica has been formed.



**Figure 5 TEM image of mesoporous silica**

Figure 5 shown a TEM image of the silica as a wormhole like material. Dark parts of the TEM image shown a solid that is the pore walls. Bright parts in the TEM image indicated a hollow space.



**Figure 6 SEM image of Cr/SM catalyst**

The analysis by Scanning Electron Microscope (SEM) was used to determine the topography and morphology of the Cr/SM catalyst was shown in Figure 6. This Figure shows that the shape of the resulting mesoporous silica partly deposited by Cr metal that possibly adhered to the surface part of the SM material.

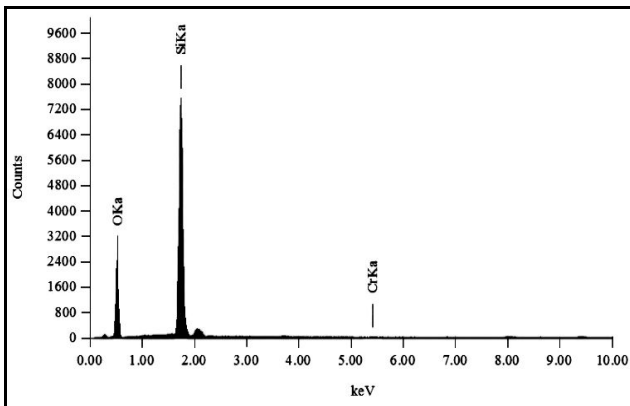


Figure 7 Spectra of EDS analysis

Analysis of Energy Dispersive Spectroscopy (EDS) in Figure 7 showed the existence of elements O, Si, and Cr with 53.11, 46.43, and 0.49 wt.%, respectively.

Figure 8 showed the adsorption-desorption isotherm curves of the SM and Cr/SM catalyst. The isotherm approach adsorption-desorption pattern of type V and the advent of a hysteresis loop of type H3. Based on the IUPAC classification, generally a type V of adsorption-desorption isotherm on the surface of mesoporous material, the adsorption tends to occur through the formation of multilayer followed by capillary condensation.

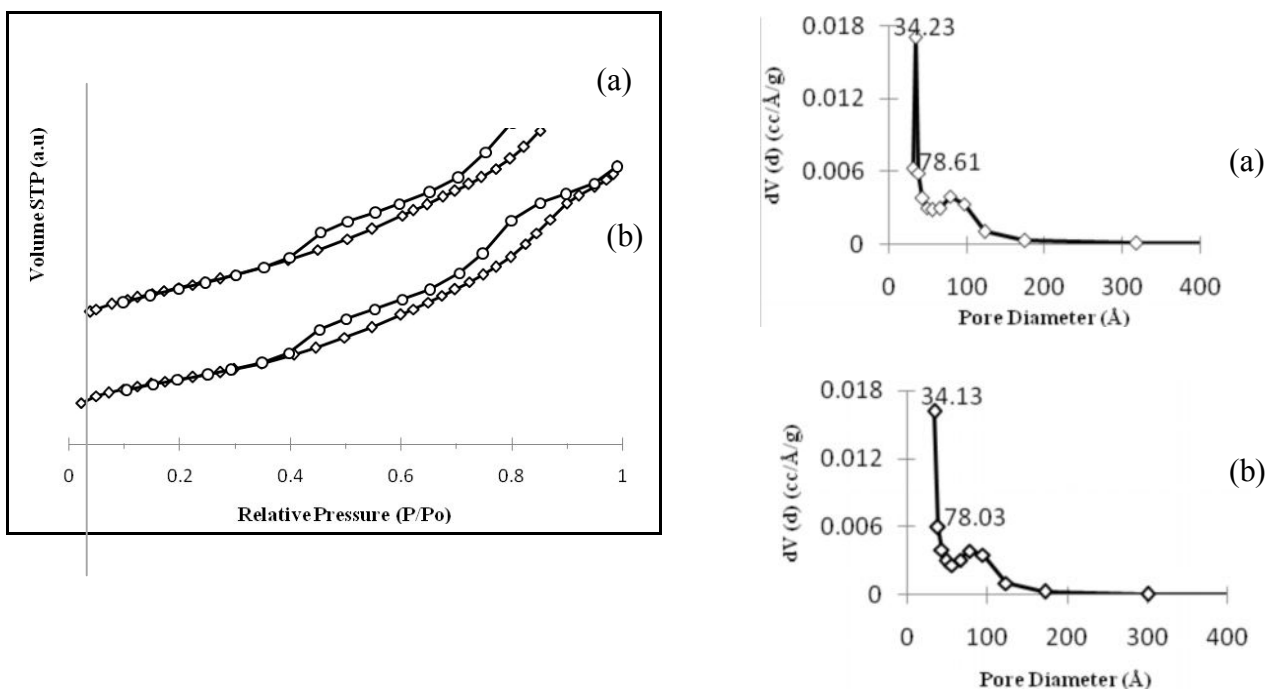


Figure 8 Adsorption-desorption isotherms of nitrogen gas (left) and the pore distribution (right) of: (a) SM and (b) Cr/S

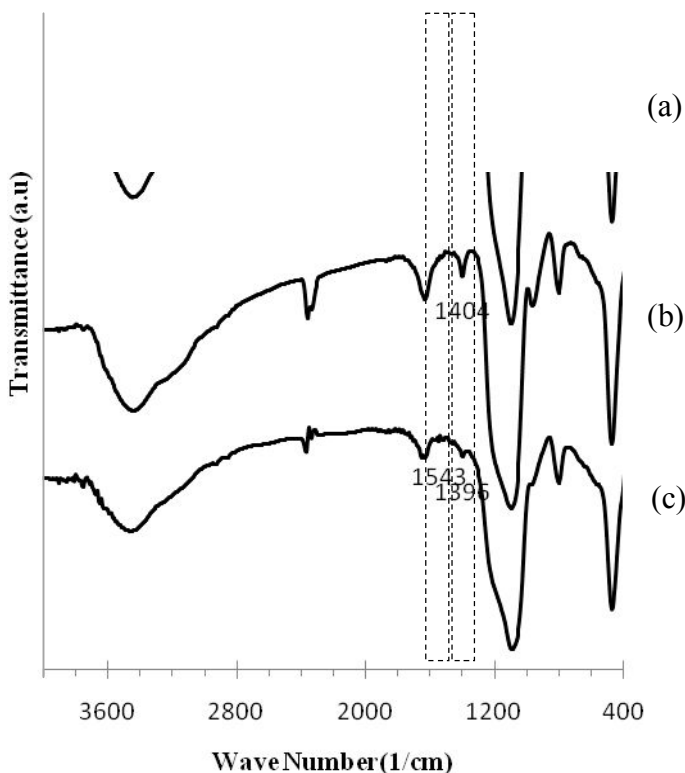
**Table 1 Porosity measurement of silica**

Sample	Surface area (m <sup>2</sup> /g) <sup>a</sup>	Pore volume (cm <sup>3</sup> /g) <sup>b</sup>	Pore diameter (nm) <sup>c</sup>
SM	279.06	0.46	3.42
Cr/SM	233.77	0.42	3.41

Description: <sup>a</sup>)the surface area is calculated by BET  
<sup>b</sup>) pore volume is determined by nitrogen adsorption at relative pressures  
<sup>c</sup>) pore diameter is calculated from BJH desorption

Table 1 showed that the the SM has a pore diameter of 3.42 nm, a surface area of 279.06 m<sup>2</sup>/g, and a pore volume of 0.46 cm<sup>3</sup>/g. The results indicated that gelatin can be used as non-ionic template to form a mesoporous silica material.

The total acid sites(measured by adsorption of ammonia as a vapor base on the acid sites of the silica) of the SM and Cr/SM were 7.85 mmol/g, and 8.20 mmol/g. The higher acid sites of the Cr/SM were supported by the addition of the Cr metal on to the SM surface.



**Figure 9 FTIR spectra of the silica: (a) SM before and (b) after adsorption of ammonia, and (c) Cr/SM after adsorption of ammonia.**

In Figure 9 (a) it appears that the mesoporous silica before adsorption of ammonia did not indicate the absorption signal of Brønsted and Lewis acid sites. Figure 9 (b) showed that the SM samples after adsorption of ammonia are emerging new absorption peak at wave number of 1404 cm<sup>-1</sup>. The absorption indicated the presence of Brønsted acid sites. Figure 9 (c) indicated the emergence of Lewis acid sites at wave number of 1543 cm<sup>-1</sup> while intensity peak of the Brønsted acid sites was decreased and the peak shift into the wave number of 1396 cm<sup>-1</sup>.

### Activity Test of Cr/SM Catalyst In Hydrocracking of Waste Lubricant

Utilization of the Cr/SM catalyst in the hydrocracking of waste lubricant produced liquid fraction higher than that of the thermal cracking as shown in Table 2. This result caused by the fact that the thermal hydrocracking was taken place via radical mechanism that produces more gas fraction than those of catalytic hydrocracking. The most effective ratio of lubricant/catalyst in producing of the liquid fraction was 75. The highest liquid product was 37.12 wt.% which consisted of gasoline and diesel oil fraction of 13.73 and 16.90 wt.% (Table 3).

**Table 2 Product distribution for the hydrocracking of lubricant oil**

Catalyst	Product distribution (wt.%)			
	Liquid fraction	Gas fraction	Coke	H <sub>2</sub> S
Thermal	21.27	75.38	3.17	0.137
Cr/SM(75)	37.12	59.62	3.09	0.101
Cr/SM(50)	33.24	61.71	4.87	0.136
Cr/SM(25)	35.67	58.84	5.31	0.126

**Table 3 Selectivity of the catalyst to the fraction of gasoline and diesel**

Catalyst	Selectivity of liquid fraction products (%-b/b)		
	Gasoline fraction	Diesel fraction	Total liquid products
Thermal	12.27	7.52	21.27
Cr/SM(75)	13.73	16.90	37.12
Cr/SM(50)	22.11	9.72	33.24
Cr/SM(25)	16.62	14.34	35.67

### Conclusion

1. Extraction of gelatine from bovine bone using acetic acid for 3 days produced gelatin in a molecular weight distribution of about 83-182 kDa.
2. Mesoporous silica has a pore diameter of 3.42 nm, the specific surface area of 279.06 m<sup>2</sup>/g, pore volume of 0.46 cm<sup>3</sup>/g, acidity of 7.85 mmol/g, and showed wormhole-like pore.
3. Cr/SM catalyst has a pore diameter, specific surface area and pore volume of 3.41 nm, 233.77 m<sup>2</sup>/g, 0.42 cm<sup>3</sup>/g, respectively, and acidity of 8.20 mmol/g.
4. The hydrocracking of lubricant in a lubricant/catalyst ratio of 75 produced highest liquid products of 37.12 wt.% with selectivity for gasoline and diesel oil fraction was 13.73 and 16.90 wt.%.

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