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CONVERSION OF OIL SHALE TO LIQUID HYDROCARBONS AS A NEW ENERGY RESOURCES USING IRON (Fe)-PILLARED CLAY (KAOLINITE) CATALYST

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ABSTRACT

In the context of new energy exploration, oil shale is currently a source of energy that is being developed so that it can be used as an alternative energy in the future. Based on this background, it is important to research the conversion method of oil shale to liquid hydrocarbons. The method used is using clay (kaolinite) catalyst and iron (Fe)-pillared clay (kaolinite) catalyst. Clay catalyst products are capable of making organic mature faster and even requiring a lower temperature for the changes (through thermal cracking of non-volatile organic material). The addition of Fe metal in the clay catalyst product to oil shale, causing the surface area of the natural clays were significantly increased, then the volume of micro pore were also increased, it causes the organic material to mature faster and the temperature required for the change is less than the shale material without Fe. The catalyst method by the pillarization technique able to increase the surface area and pore volume, thus accelerating the reaction and changing the reaction rate to be greater. It is observed that clay catalyst products can serve as catalysts for accelerating organic maturation reactions. if compared between the clay material of OD1-Ast1 (50% clay-50% organic), OD1-Ast2 (33% clay-67% organic), and the OD1-Ast3 shale material (67% clay - 33% organic),then OD1-Ast3 has a faster reaction rate. Comparison of clay material is smaller than organic, then the properties of the catalyst product to accelerate the reaction are reduced, such as the OD1-Ast2 shale material has a slow reaction rate compared to the OD1-Ast3 shale material. The addition of Fe metal in the clay catalyst product to the OD1-Ast2 shale material, resulting in OD1-Ast2-Fe shale material (75% OD1-Ast2 and 25% Fe) having a faster reaction rate than before the addition of Fe metal.The design of heavy (%) clay (kaolinite) and Fe pilaration on oil shale were greatly influence the change of TOC values when heated,then affecting maturation and Tmax. The temperature of maturation and Tmax as the main parameters of conversion of oil shale to liquid hydrocarbon. This method supports the development of science and technology in the field of exploitation and processing of natural resources.

Keywords: clay; iron (Fe)-pillared; maturation; oil shale; TOC; Tmax

INTRODUCTION

The consumption of fossil fuel is still increasing, but the oil reserves are decreasing. The serious problem faced by the Indonesian nation is the provision of energy for the next ten years, and it is predicted that oil and gas will remain an important source of primary energy, particularly to meet the needs of the transportation and industrial sectors. According to Barkia et al[1], energy supply has been a worldwide problem for the last few decades.

Many countries have sought to cope with rising oil prices and their effects on the economy. Mobilization of national energy resources becomes an important task for many countries for economic development and social progress. Al-Hamaiedh[2] said that in Jordan high oil consumption and reduction of crude oil reserves are expected to increase the energy crisis, therefore the search for alternative energy exploration becomes so important. The cost of imported energy is a burden to the national economy and there are still some countries experiencing similar problems.

Currently, exploration of new and renewable energy sources is still a top priority in the exploration of energy sources. According to Kantsler and Cook [3], oil shale contains a lot of immature organic material, when heated to a certain temperature, its organic content matures and changes physically and chemically, so as to produce new energy that is fluid hydrocarbon.

Berraja et al [4] initiated research on thermal analysis study on oil shale burning in Tarfaya. Although the methods used are not efficient yet, but the results of the study produce a fairly sophisticated heating theory today, namely pyrolysis method.

Then Bartis et al[5] conducted research by collecting oil shale, then stored in a place and burn directly to be used as a source of electrical energy. Bartis et al also did the mining of underground oil shale using space and pillar method. Burnham et al[6] continued Bartis's research by extracting the results of oil shale processing, which is done on the ground (ex-situ processing), although there were several new technologies extracting the results of underground shale processing at the site or in-situ processing .

Research on conversion technology involving oil shale heating in the absence of oxygen to the temperature at which the material decomposes into gas, condensed oil, and solid residue. This usually occurs at temperatures between 450^{O}C (842^{O}F) and 500^{O}C (932^{O}F)[7]. The decomposition process begins at a relatively low temperature (300^{O}C/570^{O}F), but faster and more complete results are obtained at higher temperatures[8].

Subono and Siswoyo[9] research on the nature of material undergoing physical, biological and chemical changes caused by heat, temperature and physical changes, based on the development of thermal technology in order to meet those needs, a new indicator is made to know the level maturity of organic materials, using thermal methods associated with geochemical technology and petrophysical parameters. The data can show the level of maturation of organic materials such as TAI, TTI, Ro, and so on.

Nagendrappa's[10] study of all clay minerals can catalyze various organic reactions occurring on the surface and interstitial spaces. The use of catalysts in industrial petroleum in recent years has undergone tremendous expansion, the most important of these catalysts used in the cracking process, as a consequence of the growth of catalytic cracking, became a major industry.

Xiufeng Xu et al [11] conducted a study by adding Ti into the organic clay, thus functioning as a catalyst of Clay-Organic. The results lead to high catalytic performance for methane combustion under reaction temperature 400^{O}C-550^{O}C. Catrinescu et al[12] presented a catalytic performance evaluation of Fe and Al based clay using powder method. Both pillared clays are very active in phenol removal, allowing the total elimination of phenol. Then Huan-Yan Xu et al[13] conducted a study of a clay catalyst based Fe-bearing that was successfully prepared and used as a heterogeneous catalyst in the Fenton system as for the acid-color change in fuchsine wastewater.

Eman and Emam [14] conducted a study of clay catalysts that have attracted much interest in catalytic applications in the petroleum industry. Clay is widely used for various processes such as catalytic cracking, hydrocracking, reformation, isomerization, hydrogenation, alkylation. The most important clays used in the manufacture of catalysts are kaolinite and monmorillonite. There are still many experts used various methods who successfully use clay as a catalyst in relation to organic,

Widjaya [15] undertook research on the development of another type of acid catalyst derived from polarized clay (bentonite) and a catalyst with two oxides (bi-oxide) in this study. Clay is used as a catalyst feedstock because it is widely available in Indonesia, and can be adjusted to a certain degree of acidity and pore size through a method of pillarization. The process of conversion of ethanol into biogasolin requires a catalyst with a sufficiently high acidity level and ranges between 2 mmol / g to 5 mmol / g. Polarized bentonite with Cr has a high acidity level of 4.09 mmol / g, whereas HZSM-5 is a commercial zeolite having 2.62 mmol / g.

Indrati et al [16] conducted a study on the determination of pellet activation energy (Th, U) Oz at the grain growth stage using dilatometer and Scanning Electrone Microscope (SEM). The method is calculated by a method based on the pellet shrinkage curve. Cahyadi et al [17] conducted a study on the behavior of ignition of Indonesian coal particles using Thermogravimetric Analysis under O2 / N2 and O2 / CO2 conditions. Sato et al [18] conducted research on free energy activation that has dependence on temperature. Temperature dependence was found to be greater for calculations. The determination of activation energy, the pre-exponential factor and the reaction rate of TGA analysis refers to some of the previous research findings, such as: Katarzyna et al[19], Himawanto[20], Himawanto et al[21], Riyanto[22], Eman A. Emam[14], Yan and Zhang[23], Sugondo[24], Sukma [25], Malika et al [26], Martono dkk [27], Suyitno [28], Minarsih [29].

The amount of shale material in Indonesia is very much, so it is expected that in the next few years there will be many sources of oil and gas available. If we wait for the process of shale material into oil and gas, it will take a long time. Therefore, it is necessary to continue research of Dewanto et al [30-33] about the process of conversion of shale material into oil and gas done in the laboratory.

In response, researchers are trying to develop new energy sources and renewable energy sources, one of which is the use of oil shale as fuel. One alternative of direct utilization of oil shale is to convert oil shale into oil and hydrocarbon gas catalytically. The use of this catalytic process is very promising because all organic material in oil shale is expected to convert all into oil and hydrocarbon gas in quick time with small Tmax value, therefore it is necessary to select suitable catalyst for the catalytic process of oil shale into hydrocarbon oil. The material used for the catalyst is clay and Fe metal. The design of heavy clay (kaolinite/illite) and Fe pilaration on oil shale greatly influenced the change of TOC values when heated thus affecting maturation and Tmax. This temperature (Tmax) as conversion parameter of oil shale to hydrocarbon oil.

In addition to Pyrolysis (TOC determination), other tests performed are SEM, XRD and TGA. The clay catalyst product can serve as a catalyst for accelerating organic maturation reactions. Clay material smaller than organic, the nature of the catalyst to accelerate the reaction becomes reduced. The level of organic maturation requires a long reaction process of three steps of reaction. Vice versa. The clay metal polarized clay catalyst product to the oil shale causes the heating process in oil shale material to have a faster reaction rate than before the Fe is added. Clay catalyst products were capable of making organic mature faster, even requiring a lower temperature for the changes (through thermal cracking of non-volatile organic material). In addition to Pyrolysis (TOC determination), other tests performed are SEM, XRD and TGA. The clay catalyst product can serve as a catalyst for accelerating organic maturation reactions. Clay material smaller than organic, the nature of the catalyst to accelerate the reaction becomes reduced. The level of organic maturation requires a long reaction process of three steps of reaction. Vice versa. The clay metal polarized clay catalyst product to the oil shale causes the heating process in oil shale material to have a faster reaction rate than before the Fe is added. Clay catalyst products are capable of making organic mature faster and even the temperature required for change (through thermal cracking of non-volatile organic material) is smaller. Clay (kaolinite) is able to decrease the activation energy (Ea) of a reaction, so it is more easily exceeded by reactant molecules consequently the reaction becomes faster. The catalyst method by the pillarization technique able to increase the surface area and pore volume, thus accelerating the reaction and changing the reaction rate to be greater.

METHOD

Research Tools

The equipment used were glassware for preparation and rock cutting equipment, X-ray Diffraction (XRD) for the distribution of oxides, TGA, SEM to determine the concentration of species/oxide characteristics, Pyrolysis, FTIR.

Main Research Materials

In this research, the materials used were oil shale (TOC≥12%) and natural clay (kaolinite/illite) obtained from the coring at a certain depth in the area of X Sumatra. Figure 1 shows coring on facies type A, B and C.

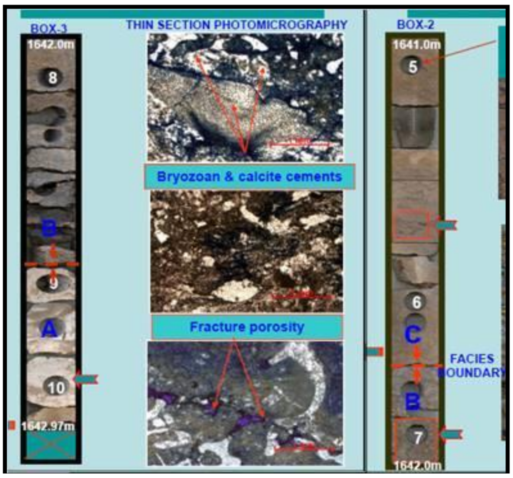


Figure 1. Type of material extracted from the Core on Facies A, B and C.

Determination of Oil Shale Material

The stage of material determination was the most important stage in material selection. Selecting the material from the drilling coring results, then grouped, namely the calcite type oil shale ($CaCO_3$) and the kaolinite or ilite oil shale group.

Characterization of Oil Shale Materials

The tools used for oil shale characterization are SEM and XRD, to determine the identity of the material. SEM for information about the state of the material, eg the type of elements present, and the distribution, topography or surface shape. XRD techniques can also model the type of compound, the percentage of the compound and its crystallographic characteristics.

TGA Test on Clay-Organic Materials

Thermogravimetry is a technique for measuring the weight change of a compound as a function of temperature or time. The result is a continuous diagram recording; schematic one-stage decomposition reactions. The two main types of thermal analysis techniques are thogogravimetric analyzers (TGAs), which automatically record changes in sample weight as a function of temperature and time, and thermal differential analysis (DTA) that measures temperature differences, T, between samples with inverted referent material as function temperature.

Pyrolysis Testing

Pyrolysis analysis was used to identify the type and maturity of shale materials as well as to detect the hydrocarbon content in shale material. The sample selected for Pyrolysis analysis is the previously destroyed sample then dried. The Pyrolysis Method consists of a temperature heater (oven) at an inert atmospheric temperature (helium) and a sample of 100 mg to determine:

a. Free hydrocarbons in the sample (clay-shale, carbonate-shale and oil shale).
b. Hydrocarbon and oxygen compounds that evaporate from the cracking process of organic material material in the sample (clay-shale, carbonate-shale and oil shale).

Maximum Temperature (Tmax)

Tmax is the maximum temperature to release hydrocarbons from the cracking process of material mixtures that occur during pyrolisis (peak S2). The recorded Tmax value is influenced by several types of material mixtures mentioned above. Thermal maturity level was measured from Tmax. For example: If the value of Tmax<435^{O}C shows the clay-shale, the above-mentioned carbonate-shale and oil shale were still immature. If the Tmax value between 435-470^{O}C indicates in the condition of thermal maturity. Whereas if Tmax> 470^{O}C indicates over mature. The pyrolysis graphic is called a pirogram.

Material Testing of Oil Shale To Liquid Hydrocarbons Conversion

To know the reaction of oil shale to liquid hydrocarbon conversion, we used some analysis and testing data on oil shale material (clay and carbonate). Tmax value were one of the chemical parameters used to determine the maturity level of oil shale. The process was part of the pyrolysis test which is the initial test of shale material in the conversion reaction. Pyrolysis analysis was also used to identify the type and maturity of shale materials as well as to detect the hydrocarbon content in shale material. Tmax is the maximum temperature for removing hydrocarbons from the cracking process of material mixtures occurring during pyrolysis (peak S2), then the oil shale has become a testable oil with a heating according to the analysis, then conducted simple combustion.

RESULTS AND DISCUSSION

Result of Material Determination

Determination of Oil Shale Material

The stage of material determination was the most important stage in material selection. Starting from coring on each known material, then grouped according to requirement. Materials needed were clay material kaolinite or ilite type.

Figure 2. Clay material that has been formed into pellets.

The clay material that has been formed into a pellet with variations in diameter size is shown in Figure 2, where the material was dry. Some clay materials used were materials with sample numbers OD1 and OD2.

Determination of Organic Materials

The selected organic material were organic material of cyclic group of compounds: naphthalene and salicylic acid and aliphatic organic compounds in the form of: stearic acid and lauric acid. Organic materials used were materials with Ast sample numbers (Stearic Acid) and Asl (Salicylic Acid). Used the organic material because it corresponds to the content present in oil shale. The amount of organic content of rocks or shale materials is usually expressed at the price of TOC (Total Organic Carbon).

Clay-Organic Material Sampling

The results of pyrolysis testing showed that organic clay (OD1-Ast, OD2-Ast) were successfully prepared as samples such as shale material, since they have the same main characteristics, as shown in Table 1.

Table 1. The results of pyrolysis testing on clay-organic synthesis and organic-carbonate synthesis.

Shale Materials (Kerogen Type II)	Clay-Organic (Synthesis)
• Shale or clay • Organic materials • TOC > 12,0%	• Clay (kaolinite/ilite) • Stearic acid • TOC ≥ 12,0%

Figure 3 shows the description of the type of material up to the processing in the laboratory, starting from the coring process, material selection, clay-organic material sampling, up to the tests. The results of pyrolysis testing on clay-organic synthesis indicate that the synthesis of the material was very good as shale material.

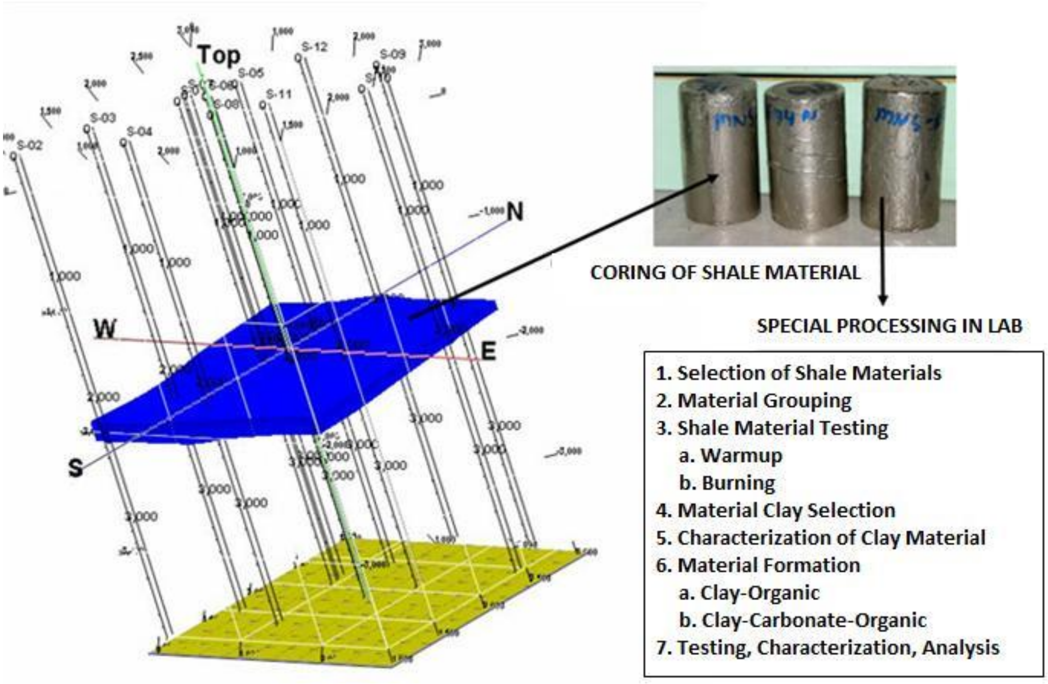


Figure 3. The coring process, starting from the determination of the type of material to the processing in the lab.

TOC (Total Organic Carbon) Test Results

TOC testing was successfully performed on clay-organic material samples (OD2-Ast). TOC test results on the shale material samples are shown in Table 3.2. This TOC values were used as one of the parameters for the initial selection stage of the material selection to be used as shale material.

Table 2. TOC (Total Organic Carbon) Test Results

Sample Name	TOC (%)
OD2-Ast1 (Clay 50% + Organic 50%)	19.94
OD2-Ast2 (Clay 33% + Organic 67%)	34.38
OD2-Ast3 (Clay 67% + Organic 33%)	11.98

Shale material can be separated between shale materials that were good or not good to serve as the basis for further processing on shale materials. Two clay-organic materials have shown excellent quality, which has TOC value of 12.0%, while an organic clay material (OD2-Ast3) shows good quality, although TOC value was only close to 12.0%, but can still be used as shale material to be tested.

Results of Analysis Using SEM

The selected shale material was characterized using SEM. The purpose was to know the morphology, particle size, material content, pores of the material and the elements contained.

SEM Analysis of Clay Material

Figure 4 shows the Edax-SEM result of clay material OD2 and Figure 5 is the result of a SEM image of clay material OD1, visible cubby shapes covered in white like snow. Such conditions indicate that the clay has the dominant kaolinite type. Seen in Figure 4 and 5 that the main constituent minerals are clay minerals.

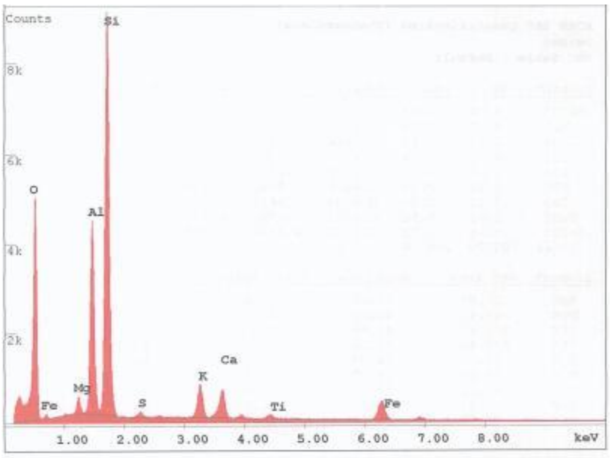
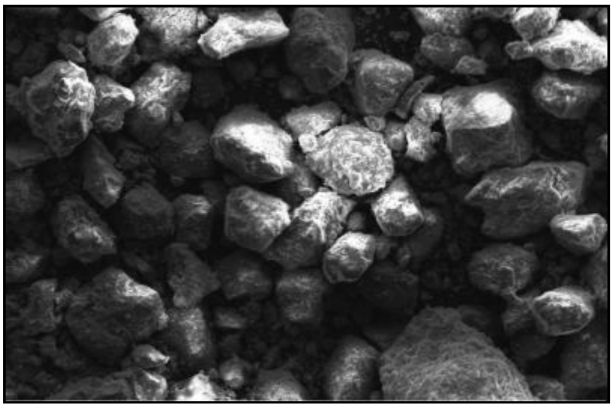
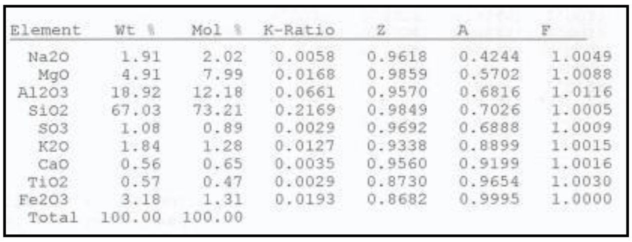


Figure 4. SEM results of clay material OD2.

In more detail the constituent is dominated by alloys of ilit and kaolinite clay, which show the texture of crenulation and hairy. Also present oil traces or oil droplets/bitumen. It also appears that the shale have undergone a diagenetic process characterized by the presence of autogenic clay minerals that form alloys of clay sheets. From the results of Edax, OD1 and OD2 materials have a very large content of Al, Si and O (dominant).





Element	Wt %	Mol %	K-Ratio	Z	A	F
Na_2O	1.91	2.02	0.0058	0.9618	0.4244	1.0049
MgO	4.91	7.99	0.0168	0.9859	0.5702	1.0088
Al_2O_3	18.92	12.18	0.0661	0.9570	0.6816	1.0116
SiO_2	67.03	73.21	0.2169	0.9849	0.7026	1.0005
SO_3	1.08	0.89	0.0029	0.9692	0.6888	1.0009
K_2O	1.84	1.28	0.0127	0.9338	0.8899	1.0015
CaO	0.56	0.65	0.0035	0.9560	0.9199	1.0016
TiO_2	0.57	0.47	0.0029	0.8730	0.9654	1.0030
Fe_2O_3	3.18	1.31	0.0193	0.8682	0.9995	1.0000
Total	100.00	100.00				

Figure 5. SEM image results of clay material OD1.

From the result of analysis by using SEM, it was known that clay morphology was kaolinite type (OD2 and OD1). Both images show a similarity that has a morphology with a large particle size and wider space, it indicates that the specific surface area was larger, so the volume of micro part was also larger. Since the nature of this clay can not expand upon contact with water, it was substantially expanded by expanding the surface area and cavities.

SEM Analysis of Organic Materials

Figure 6 shows the results of SEM and Edax image of stearic acid organic material ($C_{17}H_{35}COOH$), which is a moderately large number of chelated aliphatic (over C_{25}) compounds and most of the naphthene (cyclic chain). While the organic material salicylic acid ($C_7H_6O_2$) is shown in Figure 7.

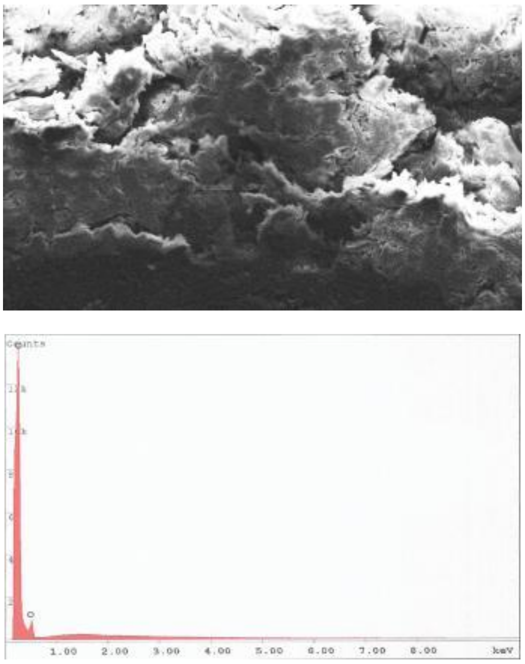


Figure 6. SEM photo results of organic material Stearic Acid (Ast).

From the Edax results, the organic material has a very large C and O content (dominant). Both organic materials were included in Kerogen type II which can be formed from several different sources of marine algae, pollen and spores, plant wax layers, fossil resins, and otherwise can also come from plant fat. This occurs as a result of the mixing of an autochton organic material in the form of phytoplankton (and possibly also zooplankton and bacteria) together with allochton material dominated by materials from plants such as pollen and spores.

This mixing shows a combination of characteristics between type I and type III kerogen. In this type of material was also often found large amounts of sulfur in cyclic chain and possibly also in sulphide bonds. The result of the SEM photo looks like a white blob that binds to each other. In this type of material was also often found large amounts of sulfur in cyclic chain and possibly also in sulphide bonds.

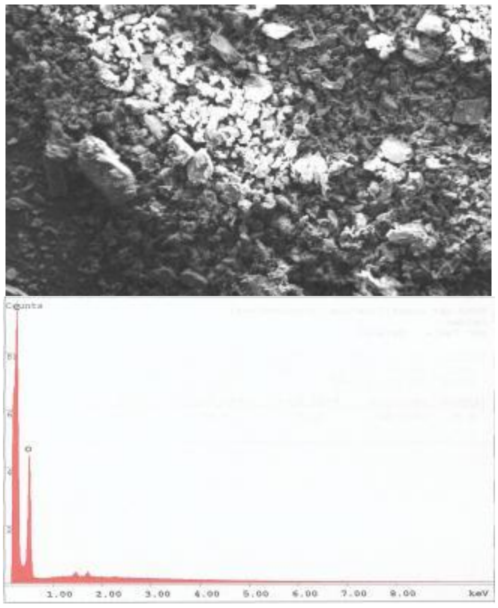


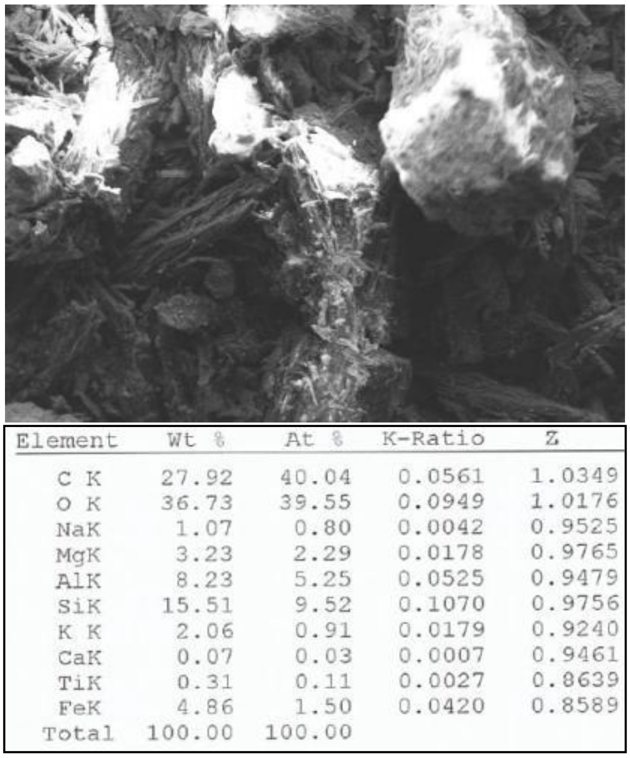
Figure 7. SEM photo results of organic material Salicylic acid (Asl).

SEM Analysis of Shale Material

After obtaining the appropriate organic container, the material was made of clay-organic OD1-Ast2, OD2-Ast2 (with 33% kaolinite mixture composition and 67% stearate acid on both sizes of the powder). Then the mixture was stirred and pressed slowly, then stored for 48 hours and stirred again and pressed again slowly, aiming for the organic material to fill evenly across the pores of the clay container material. Furthermore, the shale material was kept for at least 48 hours, the goal was for organic materials trapped (fill) pores and more binding and compact. The pores of shale material that has been filled organic become smaller, it can be indicated clay container was successfully filled / bound by organic, because it becomes smaller pores.

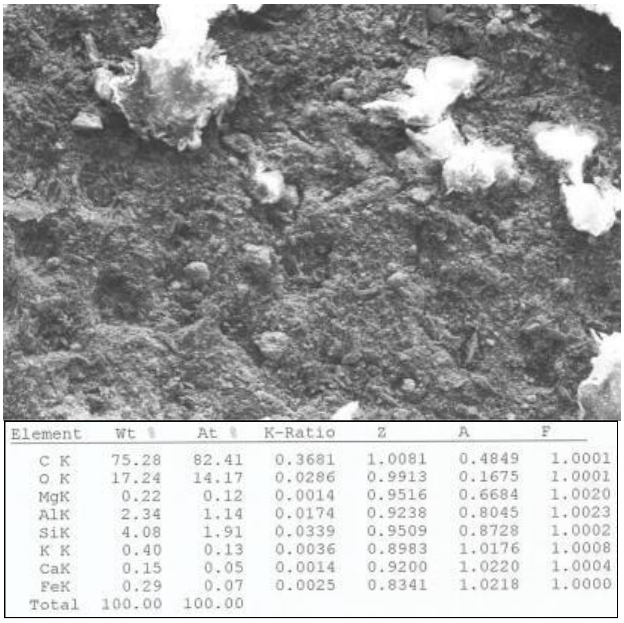
The pores were narrowed due to the organic matter and the pores were also covered by kaolinite evenly, in the picture the organic material is clearly identified, can be seen from the results of SEM analysis in Figure 8 and 9. The most important characteristic was that the shale material that has been made has a TOC value of ≥12%, which indicates the properties of a good oil shale according to the reference. With the synthesis method as mentioned above, the results obtained in Figures 8 and 9.

Clay-shale that have formed have small pores, not even seen at all, because all the pores were filled with organic material and accumulate and strongly bonded with kaolinite or some other small material percentage. The material that covered the pores that were filled with organic material, is evident in Figures 8 and 9. White color like the sky shows clay that binds strongly with organic material, so the shape of the clay shalebecomes like a clump of white cloud, which covers all the pores evenly. This condition was expected, because the clay-shale was successfully represent the oil shale to be tested for the basis of processing oil shale into crude oil (STM).



Element	Wt %	At %	K-Ratio	Z
C K	27.92	40.04	0.0561	1.0349
O K	36.73	39.55	0.0949	1.0176
NaK	1.07	0.80	0.0042	0.9525
MgK	3.23	2.29	0.0178	0.9765
AlK	8.23	5.25	0.0525	0.9479
SiK	15.51	9.52	0.1070	0.9756
K K	2.06	0.91	0.0179	0.9240
CaK	0.07	0.03	0.0007	0.9461
TiK	0.31	0.11	0.0027	0.8639
FeK	4.86	1.50	0.0420	0.8589
Total	100.00	100.00		

Figure 8. SEM image results of OD1-Ast2 material

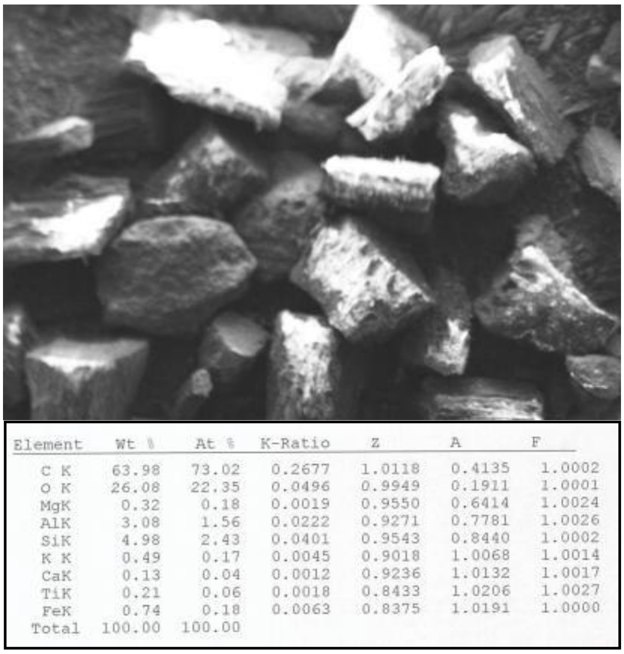


Element	Wt %	At %	K-Ratio	Z	A	F
C K	75.28	82.41	0.3681	1.0081	0.4849	1.0001
O K	17.24	14.17	0.0286	0.9913	0.1675	1.0001
MgK	0.22	0.12	0.0014	0.9516	0.6684	1.0020
AlK	2.34	1.14	0.0174	0.9238	0.8045	1.0023
SiK	4.08	1.91	0.0339	0.9509	0.8728	1.0002
K K	0.40	0.13	0.0036	0.8983	1.0176	1.0008
CaK	0.15	0.05	0.0014	0.9200	1.0220	1.0004
FeK	0.29	0.07	0.0025	0.8341	1.0218	1.0000
Total	100.00	100.00				

Figure 9. SEM image results of OD2-Ast2 material.

The results of Edax SEM of clay-shale OD2-Ast2 contain several elements with (wt,%) as follows: Carbon (75.28%), Oxygen (17.24%), Magnesium (0.22%), Aluminum (2.34%), Silicon (4.08%), Potassium (0.40%), Calcium (0.15) and Iron (0.29%). The results of Edax SEM of clay-shale OD1-Ast2 contain several elements with (wt,%) as follows: Carbon (27.92%), Oxygen (36.73%), Sodium (1.07%), Magnesium (3.23%), Aluminum (8.23%), Silicon (15.51%), Potassium (2.06%), Calcium (0.07), Ti (0.31%) and Iron (4.86%).

Then made the same clay material, ie clay-shale OD2-Ast1 (with 50% kaolinite mixture composition and 50% stearate acid on both sizes of the powder), OD1-Ast3 (with a mixture of 67% kaolinite and stearic acid 33% on both sizes of the powder). The result of the SEM image was not much different from OD1-Ast2 and OD2-ast2, the difference was only on its Edax result, ie content (wt%) in C, O and Si.



Element	Wt %	At %	K-Ratio	Z	A	F
C K	63.98	73.02	0.2677	1.0118	0.4135	1.0002
O K	26.08	22.35	0.0496	0.9949	0.1911	1.0001
MgK	0.32	0.18	0.0019	0.9550	0.6414	1.0024
AlK	3.08	1.56	0.0222	0.9271	0.7781	1.0026
SiK	4.98	2.43	0.0401	0.9543	0.8440	1.0002
K K	0.49	0.17	0.0045	0.9018	1.0068	1.0014
CaK	0.13	0.04	0.0012	0.9236	1.0132	1.0017
TiK	0.21	0.06	0.0018	0.8433	1.0206	1.0027
FeK	0.74	0.18	0.0063	0.8375	1.0191	1.0000
Total	100.00	100.00				

Figure 10. SEM image results of clay shale-Fe OD2-Ast2.

Then analyze clay shale-Fe with SEM and Edax images. From the overall results of SEM analysis on clay shale obtained SEM-Edax image results from clay-organic (clay shale) and clay shale-Fe. Both images when observed will show the difference that clay shale (see OD2-Ast2) have denser morphologies and smaller particle sizes than clay shale-Fe. clay shale-Fe have large particle sizes and their sockets were also wider, indicating that they were homogeneous and there has been a pillarization of the Fe metal, so that the specific surface area was larger, so the micro volume of the chamber was also larger. The Edax results was not differ greatly for the two materials, the only difference was in the material which arises from the Fe element more artificially, and the addition of Fe makes the surface area and pore volume larger, so it was expected to accelerate the reaction of organic changes. Comparison of SEM and Edax results of clay shale and clay shale-Fe can be seen in Figures 8, 9 and 10.

X-ray Diffraction (XRD) Measurement

The characterization of x-ray diffraction in clay-organic material aims to determine the distance of basal space (d001) of natural kaolinite and clay which has been mixed with organic material (stearic acid and salicylic acid). With the same purpose the characterization of x-ray diffraction is also done on the organic-calcite material.

Figure 11 shows graphs of XRD results of shale materials (clay-organic) OD1-Ast1, OD1-Ast2, OD1-Ast3 and OD1-Ast3-Fe. XDD test results on OD1-Ast1 shale material when viewed with HSP (High Score Plus) software for the OD1-Ast1 shale material, obtained the 2 highest peaks at different 2-theta angles.

From Figure 11 it can be seen that in the sample material (clay-organic) OD1-Ast1 has 2 peak at position 2θ 21.6470O and 26.6948O with the intensity value captured by X-ray detector was 45724.46 cts and 14014.17 cts. It can be concluded that the peak formed was the peak of the SiO2 (Tridymite low) crystals and can be known to the crystal plane or the Miller hkl indices (40-4). While at the 2nd peak was the peak of the crystals SiO2 (Quartz low) with the orientation hkl (011).

Then for samples of shale material (clay-organic) OD1-Ast2 also has 2 peak at 2θ position 21.6407O and 26.6894O with intensity value caught by X-ray detector were 63968.05 cts and 8967.09 cts. It can be concluded that the peak formed was the peak of the SiO2 (Tridymite low) crystals and can be known to the crystal plane or the Miller hkl indices (40-4). While at the 2nd peak was the peak of the crystals SiO2 (Quartz low) with the orientation hkl (011).

Then for samples of shale material (clay-organic) OD1-Ast2 also has 2 peak at 2θ position 21.6407O and 26.6894O with intensity value caught by X-ray detector were 63968.05 cts and 8967.09 cts. It can be concluded that the peak formed was the peak of the SiO2 (Tridymite low) crystals and can be known to the crystal plane or the Miller hkl indices (40-4). While at the 2nd peak was the peak of the crystals SiO2 (Quartz low) with the orientation hkl (011).

The shale material (clay-organic) OD1-Ast3 also has the 2 highest peaks (peak) at 2θ positions 21,5889O and 26.6296O with intensity values captured by X-ray detectors respectively 25422.63 cts and 19293.06 cts. It can be concluded that the peak formed was the peak of the SiO2 (Tridymite low) crystals and can be known to the crystal plane or the Miller hkl indices (40-4). While at the 2nd peak was the peak of the crystals SiO2 (Quartz low) with the orientation hkl (011).

The results of the last XRD characterization were performed on the shale material added with Fe. From Figure 11 it can be seen that in the sample material of clay (organic clay) OD1-Ast3-Fe also has two peak at the same angle position with OD1-Ast1, OD1-Ast2, and OD1-Ast3 at angles 21.6150O and 26.6665O with intensity values captured by X-ray detectors were 6800.48 cts and 1059.31 cts respectively. The peak formed was also the peak of the SiO2 (Tridymite low) crystals and can be known to the crystal plane or the Miller hkl indices (40-4). While at the 2nd peak was the peak of the crystals SiO2 (Quartz low) with the orientation hkl (011).

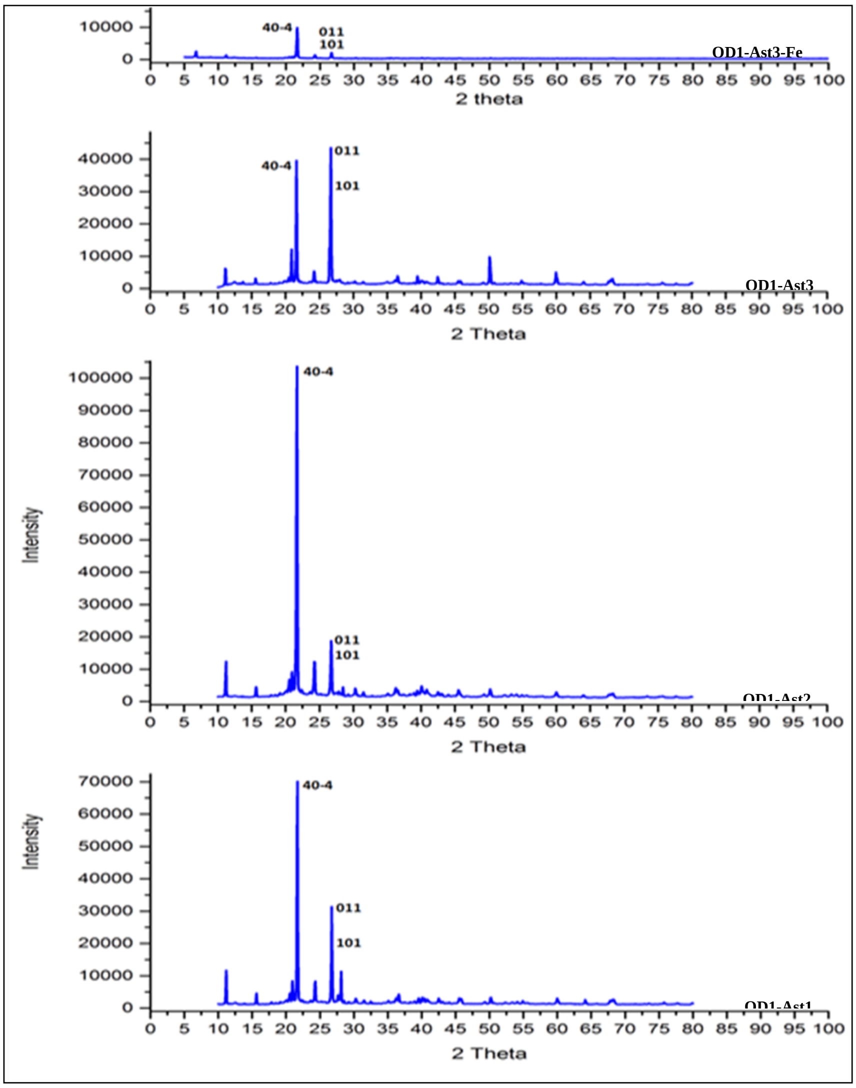


Figure 11. Result of XRD characterization of shale material (clay-organic) and +Fe.

The Result of Thermogravimetry Analysis (TGA)

Thermal analysis can be defined as measuring the physical and chemical properties of the material as a function of temperature. The two main types of thermal analysis techniques are thogogravimetric analyzers (TGAs), which automatically record changes in sample weight as a function of temperature and time, and thermal differential analysis (DTA) that measures temperature differences, T, between samples with inverted referent material as function of temperature.

The Result of TGA Test of Clay-Organic Materials (Kaolinite and C18H36O2)

Further testing with TGA was done on OD1-Ast2 material ie testing on clay shalewith mixed clay 33% composition and 67% stearic acid on both sizes of the powder. Testing of this mixture to determine the damage to the structure on the material when heated at high temperatures (more than 400^{O}C), because it can provide an overview of the process of mass changes in a material. From the results of testing with TGA, obtained graphs in Figure 12.

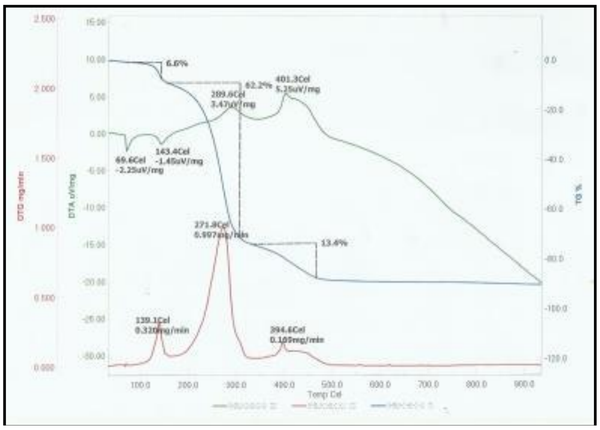


Figure 12. Graph of Thermogravimetry Analysis (TGA) of clay (OD1-Ast2).

From the results of the TGA test on OD1-Ast2 as shown in Figure above, it was found that the perfect phase change occurs at a temperature of about 305 °C, thus slightly higher than that of the perfect phase change in clay shale (OD1-Ast3). The first weight change at temperatures of about 160 ° C is the loss of water molecules contained in the crystal structure. While at a temperature of 305 ° C represents a significant second change of weight indicated was a structural change in clay material (OD1-Ast2) and the loss of water molecules chemically. When calcination was done at 470 ° C, many molecules in the clay shale (OD1-Ast2) was removed, which will affect the pore size change.

Then, a TGA test was performed on an OD1-Ast1 material that was tested on clay shale with a clay mixture composition of 50% and 50% stearate acid on both sizes of the powder. This test was performed to determine the structural damage to the material at the time of heating at high temperature (more than 400 ° C), because it can give description of the process of mass change of a material. From the test results with the TGA, the graphs obtained as shown in Figure 13.

From the results of the TGA test on clay shale as shown in Figure 13, it was found that the decrease in the percentage weight of clay shale occurred at ± 198°C temperature, indicating that the water molecule was detached from the crystal structure on the clay shale. Then another decline occurs which is a perfect phase change occurs at temperatures around ± 285°C. The first weight change was the loss of water molecules contained in the crystal structure, whereas a significant second weight change was indicated a structural change in clay shale material and the loss of water molecules chemically. The weight loss before the decline at the last temperature was indicated the maximum temperature required for clay shale to start turning into oil shale. Whereas when calcination continues until from the last decline to constant, ie, at 425°C, many molecules in the clay shale was removed, so that there was a part of the shale in the pores that are released as well. This condition was referred to as over mature, where the graph line has shown a horizontal straight tendency with increasing temperatures up to 800°C, indicating that the material has been damaged and can not be used as oil shale material. Physically it can also be seen that the material that has been calcined at temperatures above 525°C becomes blackish. Thus the temperature required for the process of converting oil shale into crude oil required an ambient temperature of ± (285°C-425°C).

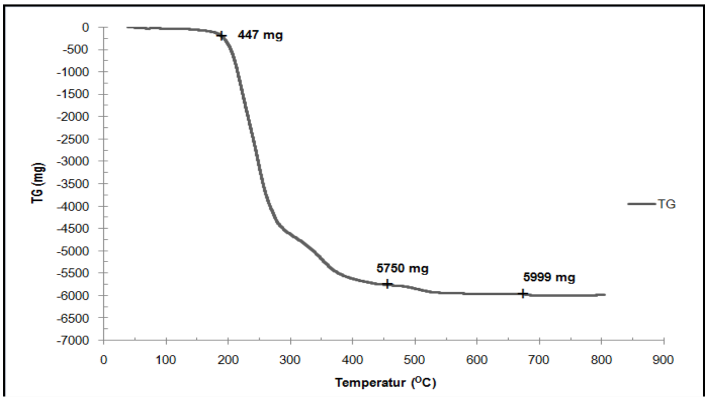


Figure 13. Graph of Thermogravimetry Analysis (TGA) of clay (OD1-Ast1)

Next, TGA testing was performed on OD1-Ast3 material that material with mixture composition of 67% clay and 33% stearic acid on both sizes of the powder. From the test results with the TGA, the graphs obtained as shown in Figure 13.

The results of the TGA test shown in Figure 13, it was found that the percentage decrease in weight of clay shale (OD1-Ast3) occurred at ± 140 ° C, indicating the water molecule detached from the crystal structure of the oil shale. Then another drop occurs which is a perfect phase change occurring at a temperature of about ± 300^{O}C

The first weight change was the loss of water molecules contained in the crystal structure, whereas a significant second weight change was indicated a structural change in oil shale material and the loss of water molecules chemically. The weight loss before the decline at the last temperature indicated the maximum temperature required for clay shale to start turning into oil shale. Whereas when calcination continues until from the last decline to constant, ie, at 400 ° C, many molecules were present in the oil shale off, so that there was a part of the shale in the pores that was released as well. This condition was referred to as over mature, where the graph line has already shown a horizontal straight tendency with increasing temperatures up to 800^{O}C, indicating that the material has been damaged and can not be used as a reference to other shale materials. Physically it can also be seen that the material has been calcined at temperatures above 600^{O}C the color becomes blackish. Thus the temperature required to process the reaction of the shale material to crude oil requires an ambient temperature between ± 300 ° C, lower than that of OD1-Ast1 ie testing on clay shale with composition of 50% clay mixture and 50% salicylic acid, and OD1-Ast2 with a mixture composition of 33% clay and salicylic acid 67%.

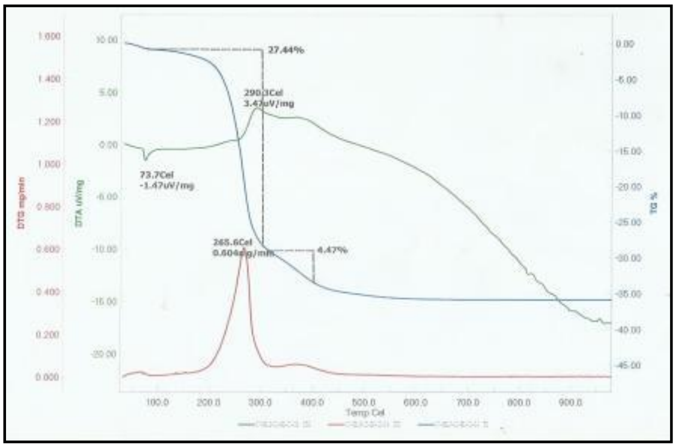


Figure 14. Graph of Thermogravimetry Analysis (TGA) of clay shale (OD1-Ast3)

TGA Test Result of Clay Material Added by Fe

The TGA test was performed on clay material (OD1-Ast2) added Fe (25%) to determine the temperature when cracking the material thermally on the material when heated at high temperatures (over 400 ° C), as it can provide an overview the process of changing the mass of a material. The test results with TGA are shown in Figure 15.

The clay material (OD1-Ast2) modified with the addition of metal material (Fe) was aimed at increasing the surface area and pore diameter, so it was expected to accelerate the reaction (the required temperature was smaller and also the time was faster). From the TGA test results on the Fe-organic clay as in Figure 15, it was found that the percentage decrease in weight occurred at ± 140 ° C temperature, indicating the water molecule detached from the crystal structure on the organic clay-Fe. Then another drop occurs which is a perfect phase change occurring at a temperature of about 290^{O}C.

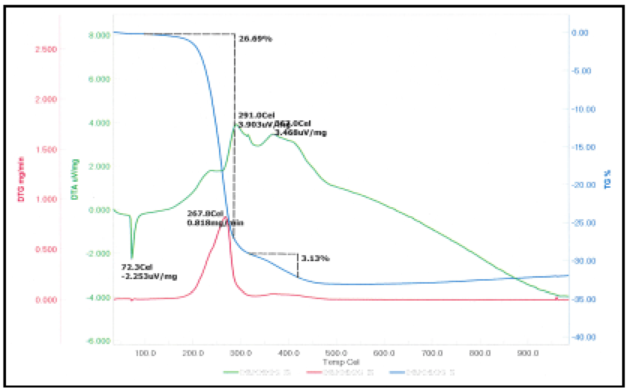


Figure 15. Graph of Thermogravimetry Analysis (TGA) for clay material (OD1-Ast2) added by Fe (25%)

The first weight change was the loss of water molecules contained in the crystal structure. While significant second-weight changes were indicated structural changes in the Fe-Clay organic material and the loss of water molecules chemically. Then calcination was done at 410^{O}C, so many of the molecules in the kaolinite-stearic acid were released, so that part of the pillar was released as well. Based on the temperature data from the TGA test apparatus, it can be seen that the heating resistance at high temperatures possessed by clay shale-Fe was less than 410^{O}C. If the calcination was done back to a temperature above 410^{O}C, then many molecules in the OD1-Ast2-Fe material were released, so that it will affect the pore size change, and the result was gas.

Oil Shale Material Heating Duration

The heating process starts from the beginning until the remaining substances that have been damaged, it turns out for two variations of mixture and addition of Fe metals require a diverse time. Figure 16 shows a graph of decreasing the mass of clay-organic samples over time. OD1-Ast3, OD1-Ast2-Fe and CEC clearly show that the three materials undergo a faster heating process than others.

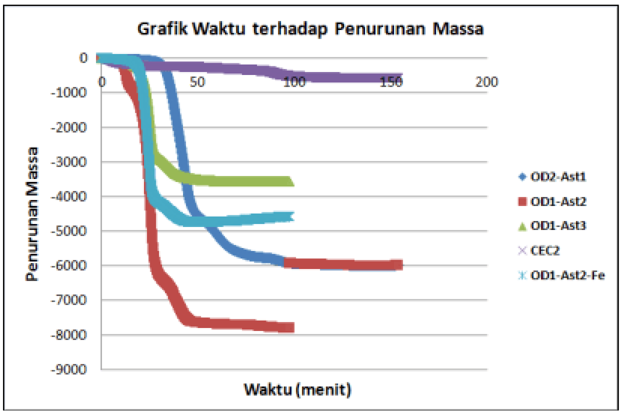


Figure 16. Graph of decline in time to reaction time on each clay-organic material and the addition of Fe.

CONCLUSION

From the results of this study, it can be concluded TOC (Total Organic Carbon) Test Result OD2-Ast1 (Clay 50% + Organic 50%) = 19.94%, OD2-Ast2 (Clay 33% + Organic 67%) = 34.38%, OD2-Ast3 (Clay 67% + Organic 33%) = 11.98%. The clay catalyst product may serve as a catalyst for accelerating organic maturation reactions. When compared with the clay material OD1-Ast1 (50% clay-50% organic), OD1-Ast2 (33% clay-67% organic), the OD1-Ast3 shale material (67% clay - 33% organic) has a reaction rate which is faster.

Comparison of clay material is smaller than organic, hence the catalyst properties to accelerate the reaction become decreased, such as OD1-Ast2 shale material has a slow reaction speed compared to OD1-Ast3 shale material, so that in the organic maturation OD1-Ast2 material requires reaction process as much three stages (long reaction). The addition of Fe metal into the clay catalyst product on the OD1-Ast2 shale material, the OD1-Ast2-Fe shale material (75% OD1-Ast2 and 25% Fe) has a faster reaction rate than before the Fe added.

CEC 2 (close to oil shale) in the heating process with clay catalyst and clay + Fe products requires a small reaction zone, because the material contains a lot of SiO2 and Al which acts as a catalyst, in addition supported also by the condition of organic materials that have begun mature.

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